VICTOR VON RICHTER'S

ORGANIC CHEMISTRY

OR

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OF THE

CARBON COMPOUNDS

EDITED BY

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PREFACE

TO THE

THIRD AMERICAN EDITION.

In the preparation of the second volume of von Richter's organic chemistry Professor Anschütz availed himself of the services of all his colleagues who were especially interested in the experimental development of the chapters considered in the present text, so that the reader may rely upon its statements, which the translator has conscientiously striven to give a simple and correct English rendering.

The preparation of the index to this volume is due to the patient and painstaking efforts of Messrs. Walter T. Taggart, Owen L. Shinn, and J. Bird Moyer, to whom the translator would here acknowledge his deep obligations for the material aid thus given him in completing a work which has extended over a period of three years.

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A TEXT-BOOK

OF

ORGANIC CHEMISTRY

II. CARBOCYCLIC COMPOUNDS.

(Compounds containing carbon rings.)

The derivatives of methane considered in the first volume consist of open carbon chains. Following these are those derivatives which have closed carbon chains or carbon rings. They are called *carbocyclic compounds*. In contrast to them are the azocyclic derivatives, which contain a ring consisting entirely of nitrogen atoms: *e. g.*, hydrazoic acid and its derivatives. The carbocyclic compounds are usually called *isocyclic derivatives*. This latter designation is, however, too comprehensive, as it includes bodies containing a ring composed of atoms of any one element at pleasure. In contradistinction to the isocyclic derivatives there are also the *heterocyclic derivatives*. In the latter, atoms of different elements have taken part in the formation of the ring (1, 78).

The carbocyclic hydrocarbons are the ring-shaped hydrocarbons, consisting of from three to seven methylene groups, which are isomeric with the olefines of like carbon content. They are either called *polymethylenes*, from the number of methylene groups present in them, or they are named after their isomeric olefines, to which is added the prefix R—*i. e.*, *R-olefines* (B. **21**, 2720 Anm.; **26**, 1085 Anm.); or, in accordance with the decision of the Geneva Conference, they take the name of the normal hydrocarbons with like carbon content, and add to the same the prefix "cyclo"—*e. g.*, *cycloparaffins*. The first and third designations are preferred.

Trimethylene [Cyclopropane]	$\begin{array}{l}CH_2\\ \vert\\ CH_2\end{array}\!>CH_2$
Tetramethylene [Cyclobutane]	$\begin{array}{l}CH_2.CH_2\\ \vert \qquad \vert\\ CH_2.CH_2\end{array}$
Pentamethylene [Cyclopentane]	$\begin{array}{l}CH_2.CH_2\\ \vert\\ CH_2.CH_2\end{array}\!>CH_2$
Hexamethylene [Cyclohexane]	$\begin{array}{l}CH_2.CH_2.CH_2\\ \vert \qquad\qquad \vert\\ CH_2.CH_2.CH_2\end{array}$
Heptamethylene [Cycloheptane]	$\begin{array}{l}CH_2.CH_2.CH_2\\ \vert\\ CH_2.CH_2.CH_2\end{array}\!>CH_2.$

Hexamethylene is also called hexahydrobenzene, and heptamethylene is known as suberane.

Consult B. **29**, 587, for the nomenclature of ring-shaped bodies.

Olefines and diolefines followed the normal hydrocarbons. In the same manner we find *cyclo-olefines*, *cyclodiolefines*, and *cyclotriolefines* attaching themselves to the *cycloparaffins*.

Benzene, of all the carbocyclic forms, demands especial consideration. It is the parent hydrocarbon of the aromatic or benzene derivatives, the most numerous of the compounds of carbon. Accepting, with Aug. Kekulé, the presence in benzene of a ring of six carbon atoms joined by an alternate single and double union to one another, then benzene would be a cyclotriolefine:

$$\text{Benzene [Cyclohexatriën] } CH\begin{matrix}\diagup CH-CH \diagdown \\ \diagdown CH=CH \diagup\end{matrix}CH.$$

The addition of hydrogen converts benzene into hexahydrobenzene, hexamethylene, or cyclohexane. The transformation products of aromatic derivatives, which can be referred to dihydro- or tetrahydrobenzene—[cyclohexadiën] and [cyclohexene]—as the parent substances, are constantly growing in number. It has become customary to consider them, in conjunction with the hexamethylene or hexahydrobenzene compounds, as *hydroaromatic derivatives*.

Many naturally occurring bodies, particularly the terpenes and camphor, belong in this group. By rigid adherence to the system just developed, every cycloparaffin system would be succeeded by a corresponding cyclo-olefine system having a like number of carbon atoms. However, in order to fully comprehend the hydroaromatic bodies, it is essential to know the aromatic compounds; therefore the discussion of the former will be deferred until the latter have been fully considered. The tricarbo-, tetracarbo-, and pentacarbocyclic compounds will be followed by the heptacarbocyclic derivatives, which are not very numerous, and lastly will appear the hexacarbocyclic compounds.

In many respects the aromatic bodies manifest a peculiar deportment, varying greatly from that of the aliphatic derivatives. However, the hydroaromatic compounds, and also the known tri-, tetra-, penta-, and heptacarbocyclic derivatives approach, in their chemical behavior, the saturated aliphatic substances, or, in case they contain pairs of doubly linked carbon atoms in the ring, they resemble the unsaturated aliphatic derivatives. Therefore, these classes of compounds, in contrast to the aromatic bodies, are designated *aliphatic-cyclic* or *alicyclic saturated* and *unsaturated compounds* (B. **22**, 769).

The study of carbocyclic derivatives has shown that the trimethylene ring can be more readily ruptured than the more stable pentamethylene or hexamethylene rings, whereas the latter are produced with greater difficulty.* It is not certain whether octocarbocyclic bodies have really been prepared.

* Similar phenomena have been encountered in the formation of certain heterocyclic aliphatic series—*e. g.*, the lactones (1, 342), the lactams (1, 358), and the anhydrides of the dicarboxylic acids (1, 429), etc.

In presenting the oxy-acids (I, 334) a representation of the spacial arrangement or configuration of the carbon atoms was given; this was intended to account for the non-formation of α- and β-lactones, in comparison with the ease with which γ- and δ-lactones are produced.

The *strain theory* of A. v. Baeyer (B. **18**, 2278; **23**, 1275) has been proposed to explain the varying stability of the tri-, tetra-, penta-, and hexamethylene rings. This theory is based on the assumption that "the four valences of the carbon atom act in lines, which connect the center of a sphere with the solid angles of a regular tetrahedron inscribed within it, and hence form an angle of 109° 28′ with each other." These four connecting lines are called the axes.

"The direction of attraction can suffer deviation; however, the magnitude of the latter has increasing tension as the consequence. The assumption of valence forces, acting at an angle, is excluded. The magnitude of the angle of deviation is the measure of the strain. In the case of ethylene the direction of attraction for the two valences of each carbon atom sustains an equally great deviation, until finally the directions have become parallel. The angle of deviation with ethylene is $\frac{109^\circ\ 28'}{2} = 54^\circ\ 44'$. With trimethylene, which may be imagined to be an equilateral triangle, the angle made by the axes equals 60°, and the deviation of each, therefore, $\frac{1}{2}(109^\circ\ 28' - 60^\circ) = 24^\circ\ 44'$."

The following deviations are obtained in a similar manner:

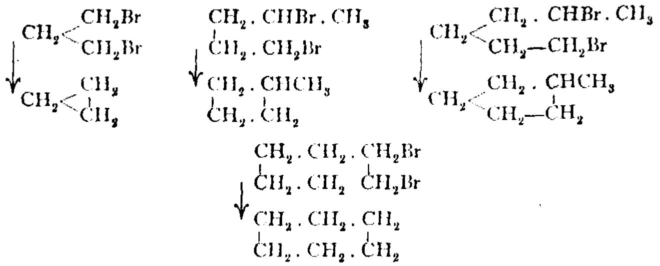
$$\text{Tetramethylene } \tfrac{1}{2}(109^\circ\ 28' - 90^\circ) = 9^\circ\ 44'$$
$$\text{Pentamethylene } \tfrac{1}{2}(109^\circ\ 28' - 108^\circ) = 0^\circ\ 44'$$
$$\text{Hexamethylene } \tfrac{1}{2}(109^\circ\ 28' - 120^\circ) = -5^\circ\ 16'.$$

It is, of course, presupposed that in the case of tetra-, penta-, and hexamethylene the carbon atoms lie in the same plane—the ring plane. The greatest deviation of the attraction of the two valences has occurred in dimethylene or ethylene. The greatest strain prevails in this body. It is the most unstable ring. It can be torn asunder not only by chlorine, bromine, and hydrogen bromide, but also by iodine. Trimethylene adds to itself with much more difficulty. Tetra-, penta-, and hexamethylene rings no longer behave like unsaturated bodies; they are quite stable in their behavior with chlorine, haloid acids, and potassium permanganate. The determination of the heat of combustion of the simplest cycloparaffins shows an appreciable fall from tri- to hexamethylene (B. **25**, R. 496), which harmonizes with the views just expressed. The strain theory of v. Baeyer would indicate that the pentamethylene ring is more readily produced than the hexamethylene ring. This conclusion was the impulse that led to the execution of a series of successful experiments resulting in the formation of pentamethylene derivatives (consult B. **28**, 655).

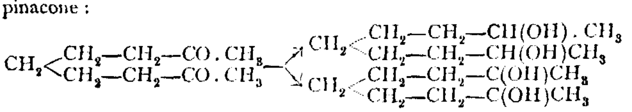
METHODS OF RING-FORMATION IN THE CASE OF CYCLO-PARAFFINS.

Methods allowing of the conversion of open carbon chains into closed carbon chains demand special consideration. *Nucleus-syntheses* were described as reactions by which carbon atoms, not previously in union with each other, were made to unite (vol. 1, 85); hence every transformation of an open chain into a closed carbon chain is a nucleus-synthesis. Indeed, there are well-known nucleus-synthetic methods which, applied to suitable aliphatic substances, lead to ring-formations with the production of cycloparaffins. These facts have already been mentioned at various places in the first volume of this book. They constitute the transition-reactions from the domain of the paraffins to that of the cycloparaffins. The most important of them are, therefore, arranged in a more tangible form:

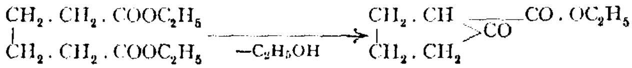
1. Cycloparaffins are produced by the action of sodium (vol. 1, 84) upon dibromparaffins—the hydrobromic acid esters of the glycols:



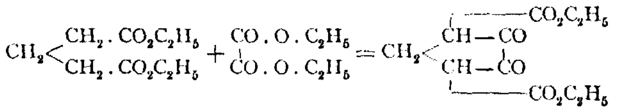
2. *Intramolecular Pinacone Formation.*—Ditertiary glycols, the pinacones, are formed, together with secondary alcohols, in the reduction of ketones. Diacetyl pentane, when reduced, yields not only an aliphatic disecondary glycol, but a ditertiary glycol, a cyclic pinacone:



3*a*. *Intramolecular Acetoacetic Ester Condensation.*—When sodium acts upon adipic ester, an intramolecular condensation corresponding to the acetoacetic ester formation takes place, and the product is a cyclic β-ketone carboxylic ester:

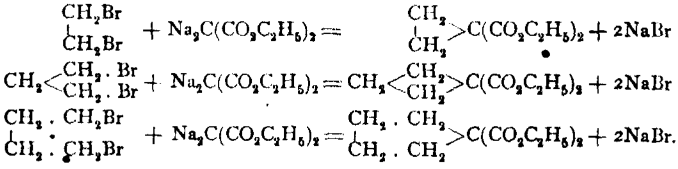


3*b*. *Oxalo-acetic Ester Condensation.*—Diketopentamethylene dicarboxylic ester results from the action of sodium ethylate upon oxalic ester and glutaric ester:



Triketopentamethylene dicarboxylic ester is similarly formed from oxalic ester and acetone dicarboxylic ester.

4. *Malonic Ester Syntheses and Acetoacetic Ester Syntheses.*—Cycloparaffindicarboxylic esters (W. H. Perkin, Jr.) result from the action of alkylen bromides upon disodium malonic esters:



This reaction has been largely applied in the preparation of numerous trimethylene derivatives by merely substituting the brom- addition products of the olefine mono- and olefine dicarboxylic esters for the alkylen bromides. Thus, when sodium acetoacetic

ester is allowed to act upon 1,4-dibrom-n-pentane, 1,2-methyl acetyl pentamethylene carboxylic ester is produced (B. **21**, 742):

$$\begin{array}{l}CH_2.CHBrCH_3\\ |\\ CH_2.CH_2Br\end{array} + 2\begin{array}{l}CHNa.CO_2C_2H_5\\ |\\ CO.CH_3\end{array} = \begin{array}{l}CH_2.CH\\ |\\ CH_2.CH_2\end{array}\!\!\begin{array}{l}\diagup CH_3\\ >CH\end{array}\!<\!\begin{array}{l}CO_2.C_2H_5\\ COCH_3\end{array} + \begin{array}{l}CH_2.CO_2C_2H_5\\ |\\ CO.CH_3\end{array} + 2NaBr.$$

aa_1-Dibrompimelic ester and sodium malonic ester form cyclopentene dicarboxylic ester, and not the expected hexamethylene tetracarboxylic ester. An exit of hydrobromic acid occurs:

$$CH_2<\begin{array}{l}CH_2—CHBr.CO_2C_2H_5\\ CH_2—CHBr.CO_2C_2H_5\end{array} \xrightarrow{-2HBr} CH_2<\begin{array}{l}CH_2—CCO_2C_2H_5\\ \quad\quad\;\; \|\\ CH_2—CCO_2C_2H_5\end{array}$$

5. When iodine or bromine acts upon the disodium compounds of the alkylen dimalonic esters, upon disodium methylene, disodium ethylene dimalonic esters, etc., the sodium is withdrawn while a ring is simultaneously produced. This is analogous to the conversion of sodium malonic ester into diacetosuccinic ester and monosodium malonic ester into dimalonic ester by means of iodine. The resulting cycloparaffin tetracarboxylic acids split off two molecules of carbon dioxide and become cycloparaffin dicarboxylic acids (W. H. Perkin, Jr.):

$$CH_2<\begin{array}{l}CNa(CO_2C_2H_5)_2\\ CNa(CO_2C_2H_5)_2\end{array} \longrightarrow CH_2<\begin{array}{l}C(CO_2C_2H_5)_2\\ |\\ C(CO_2C_2H_5)_2\end{array} \longrightarrow CH_2<\begin{array}{l}CH.CO_2H\\ |\\ CHCO_2H\end{array}$$

$$\begin{array}{l}CH_2—CNa(CO_2C_2H_5)_2\\ |\\ CH_2—CNa(CO_2C_2H_5)_2\end{array} \longrightarrow \begin{array}{l}CH_2—C(CO_2C_2H_5)_2\\ |\qquad\;\; |\\ CH_2—C(CO_2C_2H_5)_2\end{array} \longrightarrow \begin{array}{l}CH_2.CH.CO_2H\\ |\qquad\; |\\ CH_2.CHCO_2H\end{array}$$

$$CH_2<\begin{array}{l}CH_2.CNa(CO_2C_2H_5)_2\\ CH_2.CNa(CO_2C_2H_5)_2\end{array} \longrightarrow CH_2<\begin{array}{l}CH_2—C(CO_2C_2H_5)_2\\ \qquad\;\; |\\ CH_2—C(CO_2C_2H_5)_2\end{array} \longrightarrow CH_2<\begin{array}{l}CH_2.CH.CO_2H\\ \qquad\; |\\ CH_2.CHCO_2H\end{array}$$

The disodium compound of diacetyl adipic ester behaves similarly towards iodine.

6. *Cyclic Ketone Formation.*—Just as the calcium salts of the paraffin monocarboxylic acids, when heated alone, yield open-chain ketones, so do the calcium salts of some of the higher normal paraffin dicarboxylic acids afford cyclic ketones when they are subjected to dry distillation (J. Wislicenus):

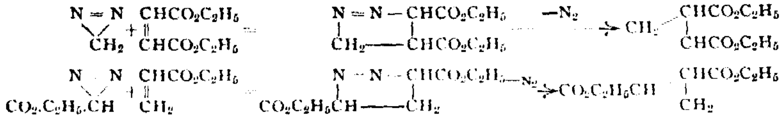
$$\begin{array}{l}CH_2.CH_2.CO_2\\ |\\ CH_2.CH_2.CO_2\end{array}\!\!>Ca \qquad CH_2<\begin{array}{l}CH_2.CH_2.CO_2\\ CH_2.CH_2.CO_2\end{array}\!\!>Ca \qquad \begin{array}{l}CH_2.CH_2.CH_2.CO_2\\ |\\ CH_2.CH_2.CH_2.CO_2\end{array}\!\!>Ca$$

$$\downarrow \qquad\qquad\qquad \downarrow$$

$$\begin{array}{l}CH_2.CH_2\\ |\\ CH_2.CH_2\end{array}\!\!>CO. \qquad CH_2<\begin{array}{l}CH_2.CH_2\\ CH_2.CH_2\end{array}\!\!>CO \qquad \begin{array}{l}CH_2.CH_2.CH_2\\ |\\ CH_2.CH_2.CH_2\end{array}\!\!>CO$$

7. Aliphatic diazo-bodies, like diazomethane and diazoacetic ester (1, 207), add themselves to olefine mono- and dicarboxylic esters, with the production of cyclic azo-derivatives or pyrazoline compounds, which

give up nitrogen quite readily and change to trimethylene compounds (E. Buchner):



I. TRI-, TETRA-, PENTA-, AND HEPTACARBOCYCLIC COMPOUNDS.

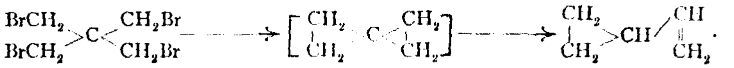
This chapter will mainly consist of the cycloparaffins and their derivatives containing the number of carbon atoms indicated above. They are distinguished from their isomeric olefines in that they possess little power (sometimes lack it entirely) of combining with the halogens and haloid acids, and are quite stable toward potassium permanganate (B. **23**, 704).

A. TRIMETHYLENE GROUP.

Trimethylene [Cyclopropane], $\begin{matrix}CH_2\\|\\CH_2\end{matrix}>CH_2$, is a readily condensible gas. It is obtained by heating trimethylene bromide with metallic sodium (*Freund*, 1882), or by the action of alcohol and zinc dust (B. **20**, R. 706).

It unites with more difficulty with bromine and hydriodic acid than propylene, $CH_2=CH.CH_3$. It is rearranged at a red heat into propylene (B. **29**, 1297). It is not oxidized by potassium permanganate (B. **21**, 1282).

Methyl Trimethylene boils at 4° (B. **28**, 22). **Vinyl Trimethylene**, $\begin{matrix}CH_2\\|\\CH_2\end{matrix}>CH.CH=CH_2$, boils at 40°; its specific gravity is 0.73. It is formed in a peculiar manner by the action of alcohol and zinc dust upon the tetra-bromhydrate of pentaerythrol:



It yields a dibromide. Potassium permanganate oxidizes it to the corresponding *glycol*, $\begin{matrix}CH_2\\|\\CH_2\end{matrix}>CH-\begin{matrix}CHOH\\|\\CH_2OH\end{matrix}$, which, by the further action of dilute nitric acid, becomes *a*-oxyglutaric acid (B. **29**, R. 780).

Monochlor-trimethylene boils at 43° (B. **24**, R. 637). **Dichlor-trimethylene** boils at 74° (B. **25**, 1954).

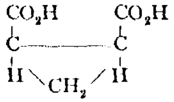
Acetyltrimethylene, $\begin{matrix}CH_2\\|\\CH_2\end{matrix}>CH.CO.CH_3$, boils at 113°. (See acetotrimethylene carboxylic acid, p. 23.)

Trimethylene Carboxylic Acids (A. **284**, 197) are obtained by the general methods 4 and 5, and also by method 7 (p. 21), which is only suitable for the preparation of trimethylene derivatives. The trimethylene polycarboxylic acids, which contain two carboxyls linked to one carbon atom, split off carbon dioxide and pass into acids containing less carboxyl. Remarkable isomeric phenomena are due to the arrangement of the carboxyl groups upon the same or different sides of the plane assumed by the trimethylene ring. This is similar to the isomerism of the trithioaldehydes (*1*, 203).

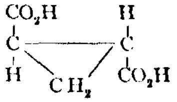
Trimethylene Carboxylic Acid, $C_3H_5 . CO_2H$, melting at 18° and boiling at 183°, is isomeric with crotonic acid. It is produced, together with butyrolactone, by heating

Trimethylene-1,1-dicarboxylic Acid (Vinaconic Acid), $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > C(CO_2H)_2$, melting at 140° (see method 4, p. 20). Hydrobromic acid converts it into brom-ethylmalonic acid, $BrCH_2 . CH_2 . CH(CO_2H)_2$. It also unites with bromine (B. **18**, 3314). It is not altered by nitric acid, potassium permanganate, or by nascent hydrogen (B. **23**, 704; **28**, 8). The esters of vinaconic acid condense to butane tetracarboxylic esters with sodium malonic ester. In this respect it deports itself like the α,β-olefine carboxylic esters (vol. 1, and B. **28**, R. 464). Consult A. **294**, 89, for the constitution of vinaconic acid and the homologue—**Methyl Vinaconic Acid.**

Trimethylene-1,2-dicarboxylic Acid is known in two isomeric modifications, called the cis- and cis-trans forms (A. **245**, 128):



l-cis form.



l-cis-trans form (1, 50).

Cis-**Trimethylene-1,2-dicarboxylic Acid** melts at 139°; its *anhydride* at 59°. The acid is produced when trimethyl-1,2-tri- and 1,2-tetracarboxylic acids are heated. Cis-trans-**Trimethylene-1,2-dicarboxylic Acid** melts at 175°; its *methyl ester*, boiling at about 210°, is obtained, together with glutaconic ester, from acryldiazoacetic ester by method 7, p. 21, and by the action of diazomethane upon fumaric ester (B. **27**, 1888; **28**, R. 290).

Trimethylene-1,2-tricarboxylic Acid, $CH_2 < \begin{matrix} C(CO_2H)_2 \\ | \\ CHCO_2H \end{matrix}$, melts at 187°, with decomposition. Its *ethyl ester*, boiling at 276°, is obtained from $\alpha\beta$ dibrompropionic ester by method 4, p. 20 (B. **17**, 1187), and from α-bromacrylic ester (B. **20**, R. 140, 258).

Sym. **Trimethylene-1,2,3-tricarboxylic Acid**, $CO_2H . CH < \begin{matrix} CH . CO_2H \\ | \\ CH . CO_2H \end{matrix}$. The cis-form melts at 150–153°; the cis-trans form melts at 220°. The *anhydride* melts at 187° and boils at 265°. The cis-acid is derived from 1,2,3-tetracarboxylic acid (B. **17**, 1652), the cis-trans form from fumaric-diazoacetic ester (B. **23**, 2583). See B. **27**, 868, for alkyltrimethylene tricarboxylic acids.

Trimethylene-1,2-tetracarboxylic Acid, $CH_2 < \begin{matrix} C(CO_2H)_2 \\ | \\ C(CO_2H)_2 \end{matrix}$, is converted at 200° into the anhydride of cis-1,2-dicarboxylic acid. Its *ethyl ester*, melting at 43° and boiling at 187° (12 mm.), is produced according to method 5, p. 21 (B. **23**, R. 241).

Trimethylene-1,2,3-tetracarboxylic Acid, $(CO_2H)_2C < \begin{matrix} CH . CO_2H \\ | \\ CH . CO_2H \end{matrix}$, passes at 95–100° into cis-1,2,3-tricarboxylic acid. Its *ethyl ester*, boiling at 246°, is obtained by method 4 (p. 20) from dibromsuccinic ester. The *cis*-1,2, *trans*-1,3-*Acid* decomposes at 196–198° (B. **28**, R. 290).

1,1-Dimethyl-2,3-trimethylene Dicarboxylic Acid, $(CH_3)_2C < \begin{matrix} CH . CO_2H \\ | \\ CH . CO_2H \end{matrix}$, is probably *caronic acid*, a decomposition product of carone, a ketone of the terpene group (see this). It can be readily changed to terebic acid (see this).

Aceto-trimethylene Carboxylic Acid, $\begin{matrix} CO_2H \\ CH_3CO \end{matrix} > C < \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}$, decomposes at 200° into CO_2 and aceto-trimethylene. Its *ester* is formed from ethylene bromide and sodium acetoacetic ester (B. **17**, 1440).

Diaceto-adipic ester results simultaneously. The ester boils at about 195°.

Methylcyclopropen-dicarboxylic Acid, $CH_3 . CH<\overset{C(CO_2H)}{\underset{C(CO_2H)}{\|}}$, melts at 200° (see B. 26, 750).

B. TETRAMETHYLENE GROUP.

The methods 1, 4, and 5, producing ring-formations, have been applied in the preparation of tetramethylene derivatives.

Methyl-tetra-methylene, $\begin{matrix} CH_2 . CHCH_3 \\ | \quad\quad | \\ CH_2 . CH_2 \end{matrix}$, boiling at 39–42°, is obtained by means of method 1, p. 20.

Amido-tetramethylene, $C_4H_7 . NH_2$, boiling at 81°, results in the action of bromine and caustic potash upon tetramethylene carbonamide. Nitrous acid changes it to

Oxy-tetramethylene, $C_4H_7 . OH$, boiling at 123°, which, acted upon with concentrated hydrobromic acid, sustains a rupture of its ring with the production of its *bromide* (boiling point, 103°) and 1,3-dibrombutane, $CH_2Br . CH_2 . CHBr . CH_3$ (J. Ch. Soc. 65, 950).

Tetramethylene-methylamine, $C_4H_7 . CH_2 . NH_2$, boiling at 83°, is prepared by reducing the nitrile of tetramethylene carboxylic acid.

Tetramethylene-methyl Carbinol, $C_4H_7 . CH(OH) . CH_3$, from the corresponding ketone, boils at 144°.

Tetramethylene-diethyl Glycol, $[C_4H_7C(OH)C_2H_5]_2$, obtained by the reduction of tetramethylene ethyl ketone, melts at 95°.

Tetramethylene-methyl- and ethyl Ketones, boiling at 135° and 145°, have been prepared from the acid chloride by action of zinc alkyls (B. 25, R. 371).

Ditetramethylene Ketone, $(C_4H_7)_2CO$, boiling at 205°, is prepared from the calcium salt of the carboxylic acid.

Tetramethylene Carboxylic Acid, $C_4H_7CO_2H$, boiling at 194°, smells like a fatty acid, and is obtained from the 1-dicarboxylic acid. Its *ethyl ester* boils at 160°; its *chloride* boils at 142°; its *anhydride* at 160°; while the *amide* melts at 130°, and the nitrile boils at 150° (B. 21, 2692).

Tetramethylene-1,1-dicarboxylic Acid melts at 155°, and then reverts to the monocarboxylic acid. Its *ethyl ester* boils at 224°, and is produced by method 4, p. 20.

Cis-**Tetramethylene-1,2-dicarboxylic Acid,** melting at 137°, is obtained from the tetracarboxylic acid. Its *anhydride* melts at 77° and boils at 271° (B. 26, 2243). The trans-acid, melting at 131° (B. 27, R. 734), is produced when the preceding acid is heated to 190° with hydrochloric acid.

Bromine and phosphorus produce 1,2-*dibromtetramethylene dicarboxylic acid*, the ester of which is converted by alcohol and potassium iodide into the ester of **Cyclobutene Dicarboxylic Acid,** $\begin{matrix} CH_2—C . CO_2H \\ | \quad\quad \| \\ CH_2—CCO_2H \end{matrix}$, which melts at 178° with decomposition, and readily changes to its *anhydride* (J. Ch. Soc. 65, 950).

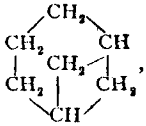
Tetramethylene-1,3-dicarboxylic Acid.—See A. 256, 198.

Diaceto-tetramethylene Dicarboxylic Ester is produced according to method 5, p. 21 (B. 19, 2048).

Tetramethylene-1,2-tetracarboxylic Acid melts at 145–150°, when it changes into the cis-1,2-dicarboxylic acid. Its *ester* is obtained by method 5, p. 21.

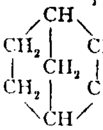
Tetramethylene-1,3-diglyoxylic Acid, $COOH . CO . CH<\overset{CH_2}{\underset{CH_2}{}}>CH . CO . COOH$, melting at 240°, is produced in the condensation of pyroracemic acid and paraformaldehyde with concentrated sulphuric acid. It is decomposed when heated with alkalies into ethylene and oxalic acid, and by concentrated sulphuric acid into a *dilactone* (B. 29, 2273).

The *truxillic acids*, found among the secondary alkaloids of cocaïne, are regarded as diphenyl tetramethylene dicarboxylic acids (see alkaloids).

See pinene for the view that it is a derivative of a combined hexa- and tetramethylene ring, , and for the argument that its decomposition products —*e.g.*, pinonic acid, pinic acid, norpinic acid—are derivatives of tetramethylene.

C. PENTACARBOCYCLIC COMPOUNDS.

The number of known pentacarbocyclic derivatives is much greater than that of the tri- and tetracarbocyclic compounds. They are derived in part from cyclopentane or pentamethylene, and in part from cyclopentenes. Cyclopentane and its derivatives have been obtained not only by the ring-synthetic methods 1, 3, 4, 5, and 6 (pp. 20, 21), but also from hexacarbocyclic ring-shaped ortho-diketones by an intramolecular atomic rearrangement—*e. g.*, benzilic acid from benzil (1, p. 54); see below—chlordiketopentamethylene. This second reaction will be again presented in the decomposition of aromatic bodies (see these). Furthermore, hexaoxybenzene has yielded remarkable pentamethylene derivatives: *croconic* acid and *leuconic* acid. They will be discussed later in connection with hexaoxybenzene.

Camphor can be readily rearranged into aromatic derivatives, and should probably be regarded as a derivative of the hydrocarbon, , which is not known. In various reactions it yields pentamethylene derivatives—*e. g.*, camphorphorone and camphoric acid. Camphor and its cyclic transformation products will not be considered until after the benzene derivatives, along with the terpenes, under the hydroaromatic bodies.

1. **Hydrocarbons. Pentamethylene,** *R-Pentene* [*Cyclo-Pentane*] $CH_2<\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}$, boiling at 50°, is obtained by the reduction of pentamethylene iodide. *Methyl pentamethylene*, boiling at 75°, is made from 1,5-dibrom-n-hexane. **1,2-Methyl-ethyl-cyclopentane** boils at 124°. **1,3-Dimethyl Pentamethylene,** from the corresponding ketone (B. 29, 403), boils at 93°.

Cyclopentene, $CH\begin{matrix}\diagup\!\!\!\!\diagup CH\ .CH_2\\ \diagdown CH_2.CH_2\end{matrix}$, boiling at 45°, is prepared by the action of caustic potash upon pentamethylene iodide (A. 275, 331), and **Perchlorcyclopentene,** C_5Cl_8, melting at 41° and boiling at 283°, by acting with PCl_5 upon perchlor-ketocyclopentenon (B. 23, 2214).

Methylcyclopentene, $CH\begin{matrix}\diagup\!\!\!\!\diagup CH\ .CH_2\\ \diagdown CH_2.CH_3\end{matrix}$, boiling at 70°, and obtained from 3-methylcyclopentanol by means of zinc chloride (B. 26, 775), yields methylglutaric acid upon oxidation.

Cyclopentadiëne, *Pentol* (B. 22, 916), $CH_2<\begin{matrix}CH=CH\\ CH=CH\end{matrix}$, boiling at 41°, is present

in the crude benzene from coal tar. It is a colorless liquid. Both acids and alkalies attack it energetically. It reduces an ammoniacal silver solution. It forms addition products with one and two molecules of the halogens and haloid acids—*e. g.*, *monochlorcyclopentene*, C_5H_7Cl, boiling at 50° (40 mm.), *trichlorcyclopentane*, $C_5H_7Cl_3$, boiling at 196°, and *tetrachlorcyclopentane*, $C_5H_6Cl_4$, boiling at 94° (15 mm.). It polymerizes readily on standing to a *dimolecular compound*, $(C_5H_6)_2$, which at the ordinary temperature boils at 170°, with partial return to the monomolecular body, and without decomposition at 88° (35 mm.). It is much more stable than the simpler compound, and recalls the terpenes in its behavior (B. 29, 552).

2. **Alcohols.—Cyclopentanol**, C_5H_9OH, boils at 139°. Its *bromide* boils at 137°, the *iodide* at 164°, and the *amine* at 107° (A. 275, 322). [3-**Methylcyclopentanol**] $HOCH<\begin{matrix}CH_2.CH.CH_3\\ | \\ CH_2.CH_2\end{matrix}$, boils at 49° (12 mm.), and the *amine* at 42° (12 mm.) (B. 25, 3519; 26, 775). Both alcohols have been prepared by the reduction of their corresponding ketones.

2-**Methylcyclopentanol**, $HO.CH<\begin{matrix}CH(CH_3).CH_2\\ | \\ CH_2\text{———}CH_2\end{matrix}$, from [methylcyclopentenon], boils at 148°.

3. **Ketones.**—The *cyclic ketones*, obtained from calcium adipate and β-methyl-adipate, according to method 6 (p. 21), constitute the starting-out material for the preparation of the corresponding alcohols, from which the saturated and unsaturated pentacarbocyclic hydrocarbons are subsequently prepared. **Adipinketone** [*Cyclopentanon*], *ketopentamethylene*, $CO<\begin{matrix}CH_2.CH_2\\ | \\ CH_2.CH_2\end{matrix}$, boiling at 130°, occurs in "wood oils," and results from the saponification of 2-ketopentamethylene carboxylic ester (p. 28). It has an odor like that of peppermint, and yields glutaric acid when it is oxidized. Its *oxime* melts at 120° (A. 275, 312). It condenses with benzaldehyde to a *mono-* and a *dibenzal* compound, $C_6H_5CH : (C_5H_6O)$ and $C_6H_5CH : (C_5H_4O) : CHC_6H_5$ (B. 29, 1601, 1836). Sodium ethylate condenses two and three molecules of cyclopentanon to *cyclopentanpentanon*, $(C_5H_6O) : (C_5H_8)$, boiling at 118° (12 mm.), and *cyclodipentanpentanon*, $(C_5H_8) : (C_5H_4O) : (C_5H_8)$, melting at 77° and boiling at 190° (12 mm.) (B. 29, 2962). 3-**Methylcyclo-pentanon**, $CO<\begin{matrix}CH_2.CHCH_3\\ | \\ CH_2.CH_2\end{matrix}$, boiling at 142° (B. 25, 3517), smells like *camphorphorone* (see this), which also, like *tanacetophorone*, belongs to the cyclopentanons. These last-mentioned phorones will be treated after camphor. A 2-**Methylcyclopentanon**, which also boils at 142–144°, has been prepared from α-methyladipic acid (B. 29, R. 1115). 2,5-**Dimethylcyclopentanon**, boiling at 146°, is obtained from $\alpha\alpha_1$-dimethyladipic acid (B. 29, 403).

1,2-**Acetylmethyl-pentamethylene**, $CH_3CO.CH<\begin{matrix}CH(CH_3)—CH_2\\ | \\ CH_2\text{———}CH_2\end{matrix}$, boiling at 170°, is obtained from the corresponding carboxylic acid (see below).

Methylcyclopentenon, $CH_3.C\begin{matrix}\nearrow CO.CH_2\\ | \\ \searrow CH.CH_2\end{matrix}$, boiling at 157°, occurs in wood-oil. Its *oxime* melts at 128° (B. 27, 1538). **Hexachlorketo-R-pentene**, $\begin{matrix}CCl_2.CCl_2\\ | \\ CCl=CCl\end{matrix}>CO$, melting at 31°, boiling at 156° (80 mm.), and $\begin{matrix}CCl.CCl_2\\ \| \\ CCl.CCl_2\end{matrix}>CO$, melting at 92° and boiling at 148° (75 mm.), result upon oxidizing the corresponding α-oxyacids, prepared from o-amidophenol and pyrocatechol, with chromic acid (B. 24, 926; 25, 2697).

Mono-, di-, and trichlor-o-diketopentamethylenes are obtained, in a manner similar to the chlorinated keto-R-pentenons, from phenol and chloranilic acid. Hydrogen sulphide converts the monochlordiketopentamethylene into *α-thiophenaldehyde* (see this), and ammonia changes it to *chlorpyridine* (B. 22, 2827). Potassium chloranilate, acted upon with chlorine or bromine and water, yields **Trichlortriketopentamethylene**,

$\begin{matrix} CO\,.\,CCl_2 \\ | \\ CO\,.\,CHCl \end{matrix}\!>\!CO$, melting at 125° (B. **25**, 848). **Tetrachlordiketo-R-pentene,** $\begin{matrix} CCl\,.\,CO \\ \| \\ CCl\,.\,CO \end{matrix}\!>\!CCl_2$, melting at 75° and boiling at 148° (27 mm.), results when resorcinol is used (p. 46) (B. **24**, 916; **25**, 2225).

The primary decomposition products of the benzenes applied in these reactions are mainly chlorinated ketonic acids—*e. g.*, in the last instance we obtained from resorcinol the acid, $CCl_3\,.\,CO\,.\,CCl:CCl\,.\,CCl_2COOH$, perchloracetyl crotonic acid, which, heated with concentrated sulphuric acid, forms the ring of ketopentamethylene (B. **26**, 513). Similarly, β,δ-dibrom lævulinic acid, $CH_2Br\,.\,CO\,.\,CHBr\,.\,CH_2\,.\,COOH$, when treated with fuming sulphuric acid, is converted into two **dibromdiketo-R-pentenes,** $\begin{matrix} CBr—CO \\ \| \\ CH—CO \end{matrix}\!>\!CHBr$, melting at 99°, and $\begin{matrix} CH—CO \\ \| \\ CH—CO \end{matrix}\!>\!CBr_2$, melting at 137° (A. **294**, 183).

Pentaketopentamethylene is *leuconic acid* (p. 25). It is produced by oxidizing *croconic acid.*

4. **Carboxylic Acids.—Cyclopentan-carboxylic Acid,** $\begin{matrix} CH_2\,.\,CH_2 \\ | \\ CH_2\,.\,CH_2 \end{matrix}\!>\!CH\,.\,CO_2H$, boiling at 214°, has a disagreeable, sweat-like odor. It has been prepared from the α-oxyacid (A. **275**, 337). **Cyclopentan-acetic Acid,** $C_5H_9\,.\,CH_2\,.\,COOH$, is an oil boiling at 140° (26 mm.). It is obtained from cyclopentanmalonic ester, the condensation product of pentamethylene iodide and sodium malonic ester (B. **29**, 1997).

2-Methylcyclopentan-carboxylic Acid, $\begin{matrix} CH_2\,.\,CH(CH_3) \\ | \\ CH_2\,.\,CH_2 \end{matrix}\!>\!CH\,.\,CO_2H$, boiling at 219°, is produced when potassium hydroxide acts upon the α-acetyl body (p. 28).

Both monocarboxylic acids may be obtained from the corresponding 1 dicarboxylic acids:

Cyclopentan-1-dicarboxylic Acid, $\begin{matrix} CH_2\,.\,CH_2 \\ | \\ CH_2\,.\,CH_2 \end{matrix}\!>\!C(CO_2H)_2$, melting at 177°, and **2-Methylcyclopentan-1-dicarboxylic Acid,** melting at 174°, whose esters have been prepared according to method 4, p. 20 (B. **26**, 2246; **27**, 1228). The *cyclopentan*-1,2-*dicarboxylic acid* is known in two modifications. The cis-form yields an anhydride. It is obtained by heating (B. **18**, 3246) the *cyclopentan*-1,2-*tetracarboxylic acid*, prepared according to method 5 (p. 21).

Cyclopentene Dicarboxylic Acid, $CH_2\!<\!\begin{matrix} CH_2—C\,.\,COOH \\ \| \\ CH_2—CCOOH \end{matrix}$, melting at 178°, results from the action of sodium alcoholate upon α,α_1 dibrompimelic acid, and by treating 1,2-dibromcyclopentan-1,2-dicarboxylic acid (produced in the bromination of cyclopentan-dicarboxylic acid) with alcohol and potassium iodide. It takes up 2Br readily. It forms adipic acid by fusion with caustic potash (B. **28**, 655).

Camphoric acid, probably 2-dimethylcyclopentan-1,3-dicarboxylic acid, will be discussed together with camphor. An ethyl cyclopentene carboxylic acid has been detected among the decomposition products of ecgonine (see this).

5. **Alcohol Carboxylic Acids.—**

α-Oxycyclopentan-carboxylic Acid, $\begin{matrix} CH_2—CH_2 \\ | \\ CH_2—CH_2 \end{matrix}\!>\!C\!<\!\begin{matrix} CO_2H \\ OH \end{matrix}$, melting at 103°, is obtained from cyclopentanon, CNH, and hydrochloric acid (A. **275**, 333). It yields pentamethylene carboxylic acid by reduction. **Hexachlor-α-oxycyclopentene carboxylic Acid,** $\begin{matrix} CCl_2—CCl_2 \\ | \\ CCl=CCl \end{matrix}\!>\!C\!<\!\begin{matrix} CO_2H \\ OH \end{matrix}$, results from the action of sodium carbonate or sodium acetate upon the chlorinated cyclohexene-o-diketone. When it is heated, it rearranges itself into an isomeric acid (B. **23**, 824). Boiling water converts both acids into *perchlorindone*, $\begin{matrix} CCl=CCl—C—CO \\ | \quad\quad\quad \| \\ CCl=CCl—C—CCl \end{matrix}\!>\!CCl$ (A. **272**, 243). **Trichlor-R-pentene**

Dioxycarboxylic Acid, $\begin{array}{l}C(OH)—CCl_2\\ \Vert \\ CCl\ —CH_2\end{array}\!\!>C\!\!<\!\!\begin{array}{l}CO_2H\\ OH\end{array}$, is produced when chlorine acts upon an alkaline phenol solution (B. **22**, 2827).

6. Ketone Carboxylic Acids.—

2-Ketopentamethylene-carboxylic Ester, $\begin{array}{l}CH_2.CH—CO_2C_2H_5\\ | \\ CH_2.CH_2\end{array}\!\!>CO$, is obtained from adipic ester by method 5 (p. 21). It forms ketopentamethylene when it is saponified. **1,2-Methylacetyl-pentamethylene-carboxylic Ester,** $\begin{array}{l}CH_2.CH(CH_3)\\ | \\ CH_2.CH_2—\end{array}\!\!>C\!\!<\!\!\begin{array}{l}CO_2C_2H_5\\ COCH_3\end{array}$, is prepared from 1,2-dibrom-n-pentane according to method 4, p. 20 (B. **21**, 742). Symmetrical **Ketopentamethylene-carboxylic Acid,** $CO\!\!<\!\!\begin{array}{l}CH_2.CHCO_2H\\ \quad\ \ | \\ CH_2.CHCO_2H\end{array}$, melting at 189°, is obtained from aconitic ester and sodium malonic ester (B. **26**, 373). **Cyclo-pentan-2,3-dion-1,4-dicarboxylic Ester,** $CH_2\!\!<\!\!\begin{array}{l}CH(CO_2C_2H_5).CO\\ \qquad\qquad\ \ |\\ CH(CO_2C_2H_5).CO\end{array}$, is produced according to method 3 (p. 20) from n-glutaric ester and oxalic ester (B. **27**, 1353). **Tri-ketocyclopentan-dicarboxylic Ester,** $\begin{array}{l}CO—CH—CO_2C_2H_5\\ | \\ CO—CH—CO_2C_2H_5\end{array}$ (with $>CO$ closing the ring), is formed from acetone dicarboxylic ester and oxalic ester (B. **29**, R. 1117). **Diphenylketocyclopentene Acetic Acid,** $\begin{array}{l}C_6H_5.C=\!=CH\\ \qquad\quad\ |\\ C_6H_5.C(OH)—CH—CH_2.COOH\end{array}$ (with $>CO$ closing the ring), is obtained from benzil and lævulinic acid.

D. HEPTACARBOCYCLIC COMPOUNDS.

The most important members of this series have been obtained from suberone. The ease with which the ring containing seven members passes into the "six-membered" ring is an argument in favor of the view that the ring-formation with carbon atoms reaches its limit with the "seven-membered" derivatives. Compare further A. **275**, 363.

Suberane, *Heptamethylene, Cycloheptane,* $\begin{array}{l}CH_2.CH_2.CH_2\\ | \\ CH_2.CH_2.CH_2\end{array}\!\!>CH_2$, boiling at 117°, results from the reduction of suberyl iodide. Bromine and aluminium bromide change suberane to pentabromtoluene (see this), whereas when it is heated with hydriodic acid, it is converted into methylcyclohexane or hexahydrotoluene (B. **27**, R. 47). **Suberylene,** *Cycloheptene,* boiling at 114°, is produced by the action of caustic potash upon suberyl iodide. Caustic potash converts its *dibromide* into **cycloheptadiëne,** *heptamethylene terpene,* C_7H_{10}, boiling at 121° (B. **29**, R. 89). **Suberyl Alcohol,** $C_6H_{12}.CHOH$, boiling at 184°, results from the reduction of suberone. Its *chloride* boils at 174°, and its *amine* at 169° (B. **26**, R. 813).

Suberone, *Cycloheptanon,* $\begin{array}{l}CH_2.CH_2.CH_2\\ | \\ CH_2.CH_2.CH_2\end{array}\!\!>CO$, boiling at 180°, has an odor like that of peppermint. It is produced in the distillation of calcium suberinate. It yields pimelic acid when it is oxidized. It condenses with benzaldehyde (B. **29**, 1600). Its *oxime* melts at 23° and boils at 230°.

Suberan-carboxylic Acid, $C_7H_{13}CO_2H$, is a colorless liquid. It results when *suberenic acid,* $C_7H_{11}CO_2H$, melting at 53°, is reduced by sodium amalgam. This latter acid is produced when alcoholic potash acts upon the liquid *chlorsuberonic acid.* The ester of **Suberane-1,1-dicarboxylic Acid** may be synthesized from hexamethylene

bromide and sodium malonic ester. It loses CO_2 and becomes suberanic acid (B. **27**, R. 735).

Oxysuberanic Acid, *Suberyl Glycollic Acid*, $C_7H_{12}(OH)CO_2H + \frac{1}{2}H_2O$, melts, when anhydrous, at 89°. It is formed when prussic acid and hydrochloric acid act upon suberone. Concentrated hydrochloric acid converts it into chlorsuberonic acid (A. **211**, 117). **1,2-Dimethyl-1,2-dihydroxyheptamethylene,** $CH_2<\begin{matrix}CH_2.CH_2.C(OH).CH_3\\CH_2.CH_2.C(OH).CH_3\end{matrix}$, is obtained from diacetyl pentane by method 2 (p. 20).

II. HEXACARBOCYCLIC COMPOUNDS.

The chemistry of the hexacarbocyclic derivatives has been much more fully and richly developed than that of the ring-systems which have been discussed in the preceding section. The hexacarbocyclic compounds are classified as follows:

A. Aromatic or Benzene derivatives containing a single nucleus.

B. Hydroaromatic substances containing a single nucleus. This class contains the *terpene* and the *camphor groups*.

C. Aromatic substances containing several nuclei. The parent hydrocarbons of this group contain (*a*) several benzene residues combined directly to each other, or by means of aliphatic hydrocarbon residues; or, (*b*) two (or more) nuclei so linked to one another that they have two carbon atoms in common (*twin nuclei, condensed nuclei*):

(*a*)	$\begin{matrix}C_6H_5\\ \vert \\ C_6H_5\end{matrix}$ Diphenyl	$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}>CH_2$ Diphenylmethane	$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}>CH.C_6H_5$ Triphenylmethane
	$\begin{matrix}C_6H_5.CH_2\\ \vert \\ C_6H_5.CH_2\end{matrix}$ Dibenzyl	$\begin{matrix}C_6H_5.CH\\ \Vert \\ C_6H_5.CH\end{matrix}$ Stilbene	$\begin{matrix}C_6H_5.C\\ \equiv \\ C_6H_5.C\end{matrix}$ Tolane, etc.
(*b*)	$\begin{matrix}C_6H_4\\ \vert \\ C_6H_4\end{matrix}>CH_2$ Fluorene	$C_{10}H_8$ Naphthalene (see this)	$C_{14}H_{10}$ Anthracene, etc. (see this).

Numerous derivatives of almost every imaginable kind can be referred to each of these hydrocarbons,—a domain of immeasurable expansibility. Many of these bodies, particularly naphthalene and its derivatives, are likewise followed by a series of hydro-bodies, which will not, however, be discussed as a fourth class, but always directly after the non-hydrogenized compounds of the respective hydrocarbon.

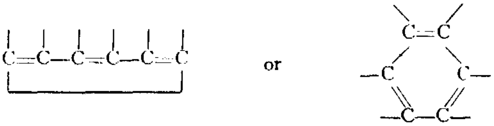
A. AROMATIC COMPOUNDS OR BENZENE DERIVATIVES CONTAINING A SINGLE NUCLEUS.

The aromatic compounds are mostly obtained from aromatic oils and resins. They differ in various respects from the members of the fatty or marsh-gas series, but are principally distinguished from the latter by their greater carbon content. The theoretical representations upon their constitution are based chiefly on the views developed by Kekulé in 1865 —Kekulé's *benzene theory.* The views of this investigator are in brief as follows (compare Kekulé, *Lehrbuch der org. Chemie,* **2,** 493; A. **137,** 129):

1. All aromatic compounds are derived from a nucleus consisting of six carbon atoms; its simplest compound is *benzene,* C_6H_6. All other aromatic derivatives may be obtained from the latter by substituting other atoms or atomic groups (side-chains) for its hydrogen atoms. The new derivatives are distinguished from the methane compounds by their specific benzene character, and are, therefore, called *benzene derivatives.*

2. Benzene has a *symmetrical* constitution. Each carbon atom is combined with one hydrogen atom. Differences between the individual C- and H-atoms have not been discovered (similar to the polymethylene derivatives). Isomerides are, therefore, only possible when two or more side-chains are present.

3. The structure of the benzene nucleus is such that the six carbon atoms, or CH-groups, form a *closed, ring-shaped* chain, the atoms being joined alternately by single and double bonds:



In benzene, C_6H_6, the fourth affinity of each C-atom is joined to hydrogen; in the benzene derivatives it is combined with other atomic groups.

THE BENZENE DERIVATIVES.

The benzene derivatives can be obtained by the replacement of hydrogen in benzene, just as the aliphatic substances can be derived from methane. Those members containing carbon side-chains can be derived from benzene, and by their decomposition, or by the splitting-off of the side-chains, they revert to benzene. The stability of the benzene nucleus distinguishes the aromatic substances from the methane derivatives. Thus, oxidation, and also reduction, which leads finally to cyclohexane derivatives or hexahydrobenzene bodies, may be carried on, as a general thing, without tearing the ring asunder. Therefore, reduction unites the benzene bodies to the cyclohexane derivatives (p. 18).

Solid benzene bodies are distinguished at the ordinary temperature by their crystallizing power. This accelerates experimental work very materially.

The hydrogen of benzene can be very readily replaced by the *halogens* and the *nitro* (NO_2) and *sulpho* (SO_3H) groups:

Chlorbenzene . . . . C_6H_5Cl	$C_6H_4Cl_2$	$C_6H_3Cl_3$ . . .	C_6Cl_6
Nitrobenzene . . . . $C_6H_5NO_2$	$C_6H_4(NO_2)_2$	$C_6H_3(NO_2)_3$	
Benzene-sulphonic acid $C_6H_5SO_3H$	$C_6H_4(SO_3H)_2$	$C_6H_3(SO_3H)_3$.	

Mono-, *di-*, *tri-*, *tetra-*, *penta-*, and *hexa*-derivatives of benzene result, depending upon whether one, two, three, four, or more of the hydrogen atoms of benzene are replaced. The production of *nitro-compounds* by the direct action of nitric acid is particularly characteristic of the benzene derivatives, whereas the fatty compounds are generally oxidized and decomposed.

In the reduction of the nitro-derivatives we obtain the *amido-compounds*:

Amidobenzene $C_6H_5.NH_2$ Aniline	$C_6H_4(NH_2)_2$	$C_6H_3(NH_2)_3$.

The so-called azo-derivatives appear as intermediate products of the reaction, whereas when nitrous acid acts on the amido-derivatives the diazo-compounds result. Both classes are of exceptional occurrence in the methane series (1, p. 172).

By introducing hydroxyl for hydrogen into benzene we obtain the *phenols*, which may be compared to the alcohols:

$C_6H_5.OH$ Phenol (Carbolic Acid)	$C_6H_4(OH)_2$ Dioxybenzene	$C_6H_3(OH)_3$ Trioxybenzene.

These resemble the tertiary alcohols in having the group C.OH attached to the three carbon affinities (1, p. 110), hence on oxidation they cannot yield corresponding aldehydes, ketones, or acids.

The benzene residue diminishes the basic properties of the amido-group and increases the acid nature of the phenol hydroxyl. It has a more *negative* character than the residues of the aliphatic hydrocarbons.

The entrance of univalent paraffin, olefine, and acetylene residues into benzene produces *homologues* of the latter, both saturated and unsaturated:

C_6H_6 Benzene	$C_6H_5CH_3$ Methyl Benzene (Toluene)	$C_6H_4(CH_3)_2$ Dimethyl Benzene (Xylene)	$C_6H_5CH_2.CH_3$ Ethyl Benzene	$C_6H_5C_3H_7$, etc. Propyl Benzene, etc.

$C_6H_5CH=CH_2$ Vinyl Benzene (Styrene)	$C_6H_5C\equiv CH$, etc. Acetenyl Benzene.

In these hydrocarbons the benzene residue preserves the specific properties of benzene; its hydrogen can readily be replaced by halogens and the groups NO_2 and SO_3H. On the other hand, the side-chains behave like the hydrocarbons of the fatty series; their hydrogen can be replaced by halogens, but not by (by action of HNO_3 or H_2SO_4) the groups NO_2 and SO_3H. Different isomeric derivatives are possible, depending upon whether the substitution of the halogens (or other groups) has occurred in the benzene residue or the side-chains—*e. g.*:

Dichlortoluene,	$C_6H_3Cl_2.CH_3$,	Chlorbenzyl chloride,	$C_6H_4Cl.CH_2Cl$,
Chlortoluene,	$C_6H_4Cl.CH_3$	Benzyl chloride,	$C_6H_5.CH_2Cl$

Benzal chloride, $C_6H_5.CHCl_2$.

The halogen atoms in the benzene residue are very firmly combined and mostly incapable of double decomposition, while those in the side-chains react exactly as in the methane derivatives.

The substitution of hydroxyl for the hydrogen of the side-chains leads to the *true alcohols* of the benzene series:

$C_6H_5 . CH_2 . OH$	$C_6H_5 . CH_2 . CH_2 . OH$	$C_6H_4<^{CH_3}_{CH_2 . OH}$
Benzyl Alcohol	Phenyl Ethyl Alcohol	Tolyl Alcohol.

The *primary* class is oxidized to *aldehydes* and *acids:*

$C_6H_5 . CHO$	$C_6H_5 . CH_2 . CHO$	$C_6H_4<^{CH_3}_{CHO}$
Benzaldehyde	Phenyl Acetaldehyde	Tolylaldehyde.

The acids in which the COOH group is joined to benzene can be formed by introducing carboxyl groups directly into benzene, or by oxidizing the homologues of the latter:

$C_6H_5 . CO_2H$	$C_6H_4(CO_2H)_2$	$C_6H_3(CO_2H)_3$
Benzene Carboxylic Acid	Benzene Dicarboxylic Acid	Benzene Tricarboxylic Acid
$C_6H_4<^{CH_3}_{CO_2H}$	$C_6H_5 . CH_2 . CO_2H$	$C_6H_3<^{(CH_3)_2}_{CO_2H}$
Toluic Acid	Phenylacetic Acid	Mesitylenic Acid.

The hydrogen of the benzene residue in these acids, as well as in the alcohols and aldehydes, is replaceable by halogens, and the groups NO_2, SO_3H, OH, etc.

Benzene is the basis in the preceding explanation. The various benzene derivatives having aliphatic side-chains are all regarded as substitution products of benzene. It is plain, however, that this manner of presentation can be reversed. Then the derivatives of benzene with *one* side-chain would be, for example, phenyl substitution products of aliphatic bodies, as indicated in the following designations:

$C_6H_5CH_3$	Phenyl methane	$C_6H_5 . CH_2 . CH_2 . OH$	Phenyl ethyl alcohol
$C_6H_5CCl_3$	Phenyl chloroform	$C_6H_5CH_2CHO$	Phenyl acetaldehyde
$C_6H_5CH_2OH$	Phenyl methyl alcohol	$C_6H_5CH_2COOH$	Phenyl acetic acid
C_6H_5COOH	Phenyl formic acid	$C_6H_5CH_2 . CH_2 . CO_2H$	Phenyl propionic acid.

ISOMERISM OF THE BENZENE DERIVATIVES.*

Proof of the Equivalence of the Six Hydrogen Atoms in Benzene.—Let any one hydrogen atom in benzene be replaced by another atom, or atomic group, and every resulting compound can exist in but one modification; thus there is but *one* chlorbenzene, *one* nitrobenzene, *one* amidobenzene, *one* toluene, *one* benzoic acid, etc. The following compounds are known in but one modification:

$$C_6H_5Cl,\ C_6H_5(NO_2),\ C_6H_5 . NH_2,\ C_6H_5 . CH_3,\ C_6H_5 . CO_2H, \text{ etc.}$$

*Theorie der aromatischen Verbindungen v. A. Ladenburg, 1876.

The six hydrogen atoms of benzene are of *equal value*, just the same as the four hydrogen atoms of methane (1, p. 37). Benzene has a *symmetrical structure*.

This equivalence of the six hydrogen atoms is very important for the theory of the benzene derivatives, and was demonstrated beyond question by Ladenburg in 1874 (B. 7, 1684; 8, 1666).

1. If phenol be converted into brombenzene, and this in turn be changed by sodium and carbon dioxide into benzoic acid, the carboxyl group of the benzoic acid will take the place of that hydrogen atom in benzene which was held by the hydroxyl in phenol. Furthermore, *three* monoxybenzoic acids are known; of these the metaoxybenzoic acid is produced from benzoic acid, while the ortho- and para-oxybenzoic acids can be converted into benzoic acid (A. 132, 151, 309). The three oxybenzoic acids (the significance of the prefixes *ortho-*, *meta-*, and *para-* will be explained further on in connection with the benzene diderivatives) yield the same phenol, which is therefore produced by the replacement of four different hydrogen atoms of benzene by the hydroxyl group. Consequently, *four* hydrogen atoms of benzene are equivalent:

	a	b	c	d	e	f	
C_6	(OH)	H	H	H	H	H	→ Phenol
C_6	Br	H	H	H	H	H	↓ Brombenzene
C_6	(CO_2H)	H	H	H	H	H	↓ Benzoic Acid ←
C_6	(CO_2H)	H	H	H	H	H	— Ortho-oxybenzoic Acid
C_6	(CO_2H)	H	H	H	H	H	↓ Meta-oxybenzoic Acid
C_6	(CO_2H)	H	H	H	H	H	— Para-oxybenzoic Acid

2. *Two pairs of hydrogen atoms are symmetrically arranged with reference to one hydrogen atom in benzene—i. e.*, the replacement of each of the two hydrogen atoms of a pair by the same atom or atomic group will give rise to the same body. This statement in regard to the one pair, *b* and *f*, is evident from the formation of the same ortho-amidobenzoic acid from the two different nitrobrombenzoic acids, which are obtained in the nitration of metabrombenzoic acid (Hübner and Petermann, A. 149, 129; 222, 111; B. 2, 140):

	a	b	c	d	e	f	
C_6	CO_2H	H	Br	H	H	H	Metabrombenzoic Acid
C_6	CO_2H	NO_2	Br	H	H	H	→ adj.-Metabromorthonitrobenzoic Acid
C_6	CO_2H	H	Br	H	H	NO_2	→ unsym-Metabromorthonitrobenzoic Acid
C_6	CO_2H	NH_2	H	H	H	H	↓ Orthoamidobenzoic Acid
C_6	CO_2H	H	H	H	H	NH_2	↓ Orthoamidobenzoic Acid.

From this it follows that a b = a f.

The proof for the second pair is found in the preparation of metabromtoluene from two bromine derivatives (Wroblewsky, A. 192, 213; A. 234, 154), in which the bromine has replaced two different hydrogen atoms, which, therefore, are symmetrically arranged: a c = a e, with reference to the hydrogen replaced by the methyl group of toluene:

	a	b	c	d	e	f			a	b	c	d	e	f
C_6	CH_3	H	H	$NH(COCH_3)$	H	H								
C_6	CH_3	H	Br	$NH(COCH_3)$	H	H	→	C_6	CH_3	H	Br	$NH(COCH_3)$	NO_2	H
C_6	CH_3	H	Br	NH_2	H	H		C_6	CH_3	H	Br	H	NO_2	H
C_6	CH_3	H	Br	H	H	H		C_6	CH_3	H	H	H	NH_2	H
C_6	CO_2H	H	Br	H	H	H	←	C_6	CH_3	H	H	H	Br	H

When this bromtoluene is oxidized it changes to the same metabrombenzoic acid which is employed as the starting-out material for the preparation of the adj.- and unsym.-metabromorthonitrobenzoic acid. Hence it follows that in the latter proof the bromine replaces two different hydrogen atoms from those previously replaced by the amido group of the orthoamidobenzoic acid, and, consequently, there are present in benzene not only one, but also two pairs of hydrogen atoms, which are symmetrically arranged with reference to one hydrogen atom, which would thus prove the equal value of the six hydrogen atoms in benzene (compare also Ladenburg, B. **10**, 1218).

The proof of the symmetrical arrangement of the second pair of hydrogen atoms may be added to the preceding presentations in regard to the first pair. It is as follows: Orthoamidobenzoic acid, obtained in two different ways (p. 33), can be changed to the same oxybenzoic acid—salicylic acid. When the latter is nitrated it yields two different mononitrosalicylic acids. On heating the diethyl ethers of these acids with ammonia, both ethoxyl groups are replaced by amido-groups, and free nitroamidoacids are then liberated from the nitroamidobenzamides. Nitrous acid and alcohol change the nitroamidobenzoic acids into the same nitrobenzoic acid. As this acid, obtained from the two different nitrosalicylic acids, yields an amidobenzoic acid (meta), which differs from the amidobenzoic acid that gave the salicylic acid, and as it affords an oxybenzoic acid (meta), differing from salicylic acid, there must be two additional hydrogen atoms in benzene which are symmetrically arranged with reference to the one replaced by the CO_2H group:

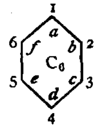
	a	b	c	d	e	f			a	b	c	d	e	f
C_6	CO_2H	NH_2	H	H	H	H	=	C_6	CO_2H	H	H	H	H	NH_2
C_6	CO_2H	OH	H	H	H	H	=	C_6	CO_2H	H	H	H	H	OH
C_6	CO_2H	OH	NO_2	H	H	H		C_6	CO_2H	H	H	H	NO_2	OH
C_6	CO_2H	NH_2	NO_2	H	H	H		C_6	CO_2H	H	H	H	NO_2	NH_2
C_6	CO_2H	H	NO_2	H	H	H	=	C_6	CO_2H	H	H	H	NO_2	H
C_6	CO_2H	H	NH_2	H	H	H	=	C_6	CO_2H	H	H	H	NH_2	H
C_6	CO_2H	H	OH	H	H	H	=	C_6	CO_2H	H	H	H	OH	H

But one place, therefore, remains for the third oxybenzoic acid, the paraoxybenzoic acid, and this place—the so-called para-place or position—is possible only once in benzene.

The six hydrogen atoms of benzene are, therefore, equal, and, as two pairs of hydrogen atoms, symmetrically arranged with reference to one hydrogen atom, are present in benzene, *a disubstitution product of benzene cannot occur in more than three isomeric forms.*

Basis of the Determination of Position of the Benzene Substitution Products.—The equal value of the six hydrogen atoms

of benzene finds expression in the hexagon formula proposed for benzene. In showing this the mutual linkage of carbon atoms in the benzene ring can remain in the background. It is very obvious that every diderivative, $C_6H_4X_2$, resulting from the replacement of two hydrogen atoms can exist in three distinct modifications. Their isomerism is dependent upon the relative position of the two groups entering the benzene. This kind of isomerism is designated isomerism of position or place (1, 43). In fact, three modifications are known of most of the diderivatives. In no instance are more than three known. Thus there are three



$C_6H_4<^{OH}_{OH}$	$C_6H_4<^{Br}_{NO_2}$	$C_6H_4<^{NH_2}_{NH_2}$	$C_6H_4<^{OH}_{NO_2}$
Dioxybenzenes	Bromnitrobenzenes	Diamidobenzenes	Nitrophenols.
$C_6H_4<^{CO_2H}_{OH}$	$C_6H_4<^{CH_3}_{CH_3}$	$C_6H_4<^{CO_2H}_{CH_3}$	$C_6H_4<^{CO_2H}_{CO_2H}$
Oxybenzoic Acids	Dimethyl Benzenes	Toluic Acids	Phthalic Acids, etc.

The three modifications of each of these compounds may be transformed into the corresponding modifications of the other. Hence, if the relative position of the substituting atoms or atomic groups of the three modifications of one of these bodies has been determined, it is then known for all the others, which can be converted into the three modifications of the first body by easy reactions, *unaccompanied by intramolecular atomic rearrangements.*

It has been possible to ascertain the opposing position of the substituting groups,—*e. g.*, for the three dibrombenzenes, the three diamidobenzenes, and for the three phthalic acids,—and thus a basis has been obtained for the arrangement of the other disubstitution products into three series, which have been distinguished as the *ortho-*, *meta-*, and *para-series.*

In the *ortho-compounds* two adjacent hydrogen atoms of benzene have been replaced. Indicating the six hydrogen atoms with numbers or letters, and arbitrarily making any one of them 1 or a, it will be obvious that two ortho-positions are present: a, b = a, f or 1, 2 = 1, 6 b (2) and f (6) are symmetrical with reference to a (1). The *meta-bodies* result from the substitution of the hydrogen atoms a, c = a, e or 1, 3 = 1, 5. The positions c (3) and e (5) are symmetrical to a (1). The *para-compounds* arise from the substitution of the hydrogen atoms a, d or 1, 4. The ortho- and meta-places have two positions of equal value, 5 and 6, also 3 and 5, while the para position has only 4 to 1.

The position of the substituting groups in diderivatives is indicated by the prefixes ortho-, meta-, and para- before the names of the compounds. These are usually abbreviated to o-, m-, p-, or to numbers included in brackets and placed before the names: [1,2]-, [1,3]-, [1,5]-. The formula is usually written so that an hexagon expresses the benzene ring, and the combined atoms or atomic groups are attached to the six angles of the hexagon.*

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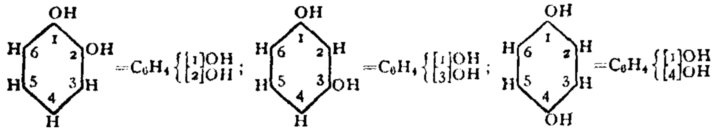
* Dr. Siegfried Pfaff has suggested a simpler method of writing. He replaces the

Or, by inserting the designation of position in the ordinary formulas between the benzene residue and the substituting groups—*e. g.* :



Pyrocatechol o-Dioxybenzene [1, 2]-Dioxybenzene	Resorcinol m-Dioxybenzene [1, 3]-Dioxybenzene	Hydroquinone p-Dioxybenzene [1, 4]-Dioxybenzene.

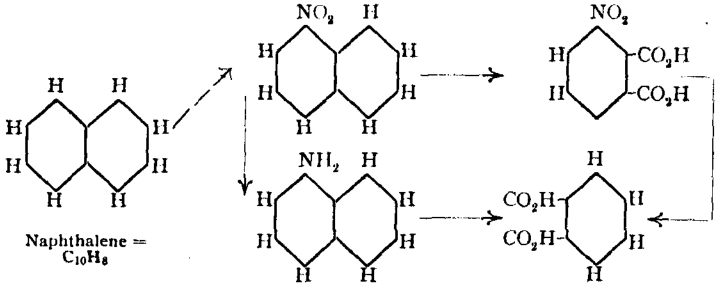
The following substances may also be mentioned as chief representatives of the three isomeric series:

	Ortho, [1,2].	Meta, [1,3].	Para, [1,4.]
$C_6H_4<^{OH}_{CO_2H}$	Salicylic Acid.	Metaoxybenzoic Acid.	Paraoxybenzoic Acid.
$C_6H_4<^{CH_3}_{CH_3}$	Orthoxylene.	Isoxylene.	Paraxylene.
$C_6H_4<^{CO_2H}_{CO_2H}$	Phthalic Acid.	Isophthalic Acid.	Terephthalic Acid.

Determination of the Positions in Diderivatives.—Dismissing for the moment the mutual linkage of the six carbon atoms, the benzene hexagon permits of the prediction of two chemically identical ortho-, two meta-, and one para-derivatives. The constitution of the three phthalic acids or benzene dicarboxylic acids is evident from the following facts (B. 4, 501):

The phthalic acid resulting from the oxidation of naphthalene is the [1, 2], or ortho-benzene dicarboxylic acid. Naphthalene consists of two benzene nuclei, which have in common two C-atoms holding the ortho-position.

The oxidation of nitronaphthalene produces nitro-o-phthalic acid, which can be changed to phthalic acid. o-Phthalic acid results from the oxidation of amidonaphthalene, formed from nitronaphthalene. This is because the oxidation at one time destroys the one and then the other side of the naphthalene molecule. It shows, further, the constitution of naphthalene, and, again, the constitution of phthalic acid as the o-dicarboxylic acid of benzene:



Naphthalene = $C_{10}H_8$

α-Amidonaphthalene

Benzene-o-dicarboxylic Acid, Phthalic Acid.

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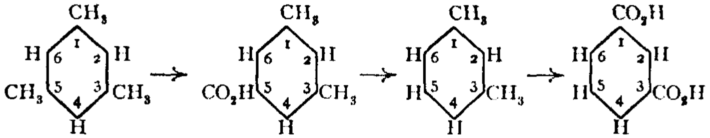
hexagon by a horizontal line and then distributes the six atoms or atomic groups in the following manner:

$NO_2\frac{NO_2 \quad H}{H \quad\; H}H$, $NH_2\frac{H \quad H}{H \quad H}N=N\frac{H \quad H}{H \quad H}H$

o-Dinitrobenzene p-Amidoazobenzene.

Isophthalic acid is benzene-m-dicarboxylic acid, as it can be obtained by the oxidation of isoxylene. The latter is m-dimethylbenzene. This is proved by its formation from mesitylenic acid, the first oxidation product of mesitylene, the [1,3,5] trimethylbenzene:



Mesitylene [1,3,5]-Trimethylbenzene — Mesitylenic Acid — Isoxylene [1,3]-Dimethylbenzene — Isophthalic Acid, Benzene-[1,3] dicarboxylic Acid.

Ladenburg demonstrated that mesitylene was really [1,3,5]-trimethylbenzene, in that he proved the three non-substituted hydrogen atoms of the mesitylene to be of equal value (A. 179, 174):

		a	b	c			a	b	c	
C_6	$(CH_3)_3$	H	H	H						
↓ C_6	$(CH_3)_3$	NO_2	NO_2	H						
↓ C_6	$(CH_3)_3$	NO_2	NH_2	H →	C_6	$(CH_3)_3$	NO_2	H	H	
↓ C_6	$(CH_3)_3$	NO_2	$NHCOCH_3$	H	↓ C_6	$(CH_3)_3$	NH_2	H	H	
↓ C_6	$(CH_3)_3$	NO_2	$NHCOCH_3$	NO_2	↓ C_6	$(CH_3)_3$	$NH(COCH_3)$	H	H	
↓ C_6	$(CH_3)_3$	NO_2	NH_2	NO_2	↓ C_6	$(CH_3)_3$	$NHCOCH_3$	NO_2	H	or
↓ C_6	$(CH_3)_3$	NO_2	H	NO_2	↓ C_6	$(CH_3)_3$	NH_2	NO_2	H	or
		b = c					a = b			

		a	b	c
C_6	$(CH_3)_3$	$NHCOCH_3$	H	NO_2
↓ C_6	$(CH_3)_3$	NH_2	H	NO_2
		a = c		

The course of the proof is evident from the preceding diagram. Mesitylene yields dinitromesitylene, the NO_2 group of which may replace the hydrogen atoms *a* and *b*. From it we get nitroamido-, nitroacetamido-, dinitroacetamido-, dinitroamido-, and dinitromesitylene, identical with the starting-out substance; consequently *b* and *c* are of equal value. Nitroamidomesitylene, in which it is assumed that the NH_2 group occupies the position *b*, yields mononitro-, monoamido-, monoacetamido-, monoacetamidonitro-, monoamidonitromesitylene, identical with the first nitroamidomesitylene obtained by reduction of dinitromesitylene; hence *a* and *b*, or *a* and *c*, are of equal value, but, as *b* and *c* are considered as of equal value, the equivalence of the three nonsubstituted hydrogen atoms of mesitylene is proved. Mesitylene is symmetrical, therefore the three methyl groups in it must occupy the position [1, 3, 5].

The position [1-4] is all that remains for the third benzene dicarboxylic acid, terephthalic acid. This can be proved in the following manner: Terephthalic acid is obtained from p-dimethyl benzene, and the latter from p-bromtoluene (by means of methyl iodide and sodium). By oxidation p-bromtoluene yields p-brombenzoic acid. p-Brombenzoic acid and p-oxybenzoic acid belong in the same series, as p-oxybenzoic acid can be made from the same p-amidobenzoic acid, by means of the diazo-compound, from which p-brombenzoic acid can be prepared. But it was shown in the preceding paragraphs, in regard to p-oxybenzoic acid (p. 34) that its hydroxyl group replaced an

hydrogen atom which was not arranged symmetrically with reference to any other hydrogen atom in benzene.

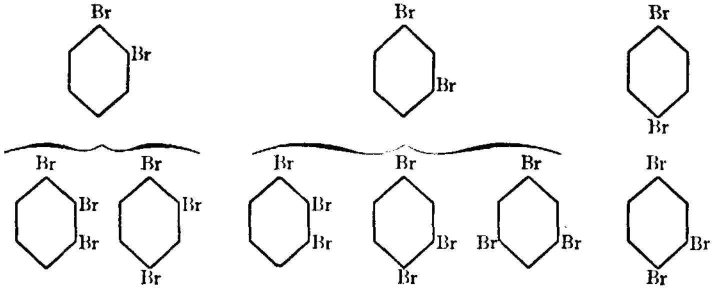
The three phthalic acids bear a genetic relationship to the diderivatives of benzene, which do not contain carbon-containing radicals as substituents. The three dinitrobenzenes can be changed to nitroamido-, bromnitro-, bromamido-, and dibrombenzenes on the one hand, and, upon the other, into nitrocyan-, nitrocarboxyl-, amidocarboxyl-, cyancarboxyl-, and phthalic acids by reactions, in which intramolecular atomic rearrangements have not been observed (B. 18, 1492, 1496):

$$C_6H_4<^{NO_2}_{NO_2} \rightarrow C_6H_4<^{NO_2}_{NH_2} \rightarrow C_6H_4<^{NO_2}_{Br} \rightarrow C_6H_4<^{NH_2}_{Br} \rightarrow C_6H_4<^{Br}_{Br}$$

$$\swarrow$$

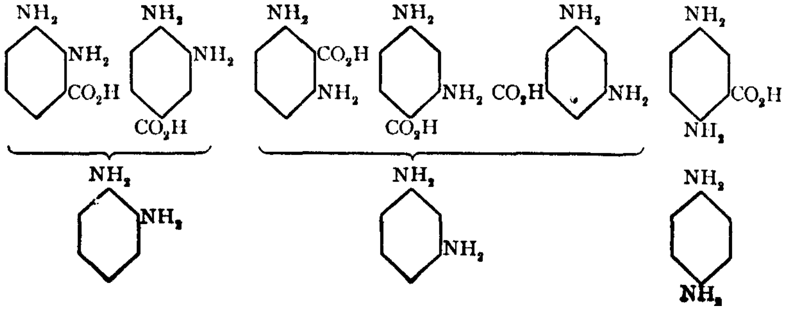
$$C_6H_4<^{NO_2}_{CN} \rightarrow C_6H_4<^{NO_2}_{CO_2H} \rightarrow C_6H_4<^{NH_2}_{CO_2H} \rightarrow C_6H_4<^{CN}_{CO_2H} \rightarrow C_6H_4<^{CO_2H}_{CO_2H}$$

W. Körner, in 1874 (Gazz. chim. ital. 4, 305), proved the position of the substituents in the three dibrombenzenes in an entirely different way. This was also done for the three diamidobenzenes in 1872 by P. Griess (B. 5, 192; 7, 1223). The results are concordant among themselves, and agree with that obtained in previous demonstrations. Körner showed that by converting the three known dibrombenzenes into tribrombenzenes the first dibrombenzene would furnish *two* dibrombenzenes, the second *three* different tribrombenzenes, and the third but *one* tribrombenzene. Proceeding from the benzene hexagon, Körner concluded that the first dibrombenzene contained its bromine atoms in the ortho-position, the second in the meta-, and the third in the para-positions. This view is plainly seen in the subjoined diagram. The hydrogen atoms are omitted for the sake of clearness:



The reverse of this proof, if it may be so styled, is found in the idea which P. Griess carried out experimentally.

There are six isomeric diamidobenzoic acids. The diamidobenzene which results from two of these acids by the exit of carbon dioxide is the o-compound, that one which is formed from three of the acids is the m-body, and the product from the sixth acid is the para-derivative:



Further evidence is found in the derivatives of the three isomeric xylenes, thus:

Metaxylene yields 3 nitroxylenes, xylidines, and xylenols,
Orthoxylene yields 2 nitroxylenes, xylidines, and xylenols,
Paraxylene yields 1 nitroxylene,

from which it may be concluded that meta- or isoxylene and isophthalic acid have the position [1,3], orthoxylene and phthalic acid the position [1,2], and paraxylene and terephthalic acid the position [1,4] (B. **18**, 2687).

That two adjacent carbon atoms of the benzene nucleus do indeed carry the side-groups in the ortho-compounds is further obvious from their ability to enter simple reactions, in which, by union of the side-chains, there result carbo- and, particularly, hetero-cyclic condensation products (compare o-phenylenediamine, o-amidophenol, o-amidothiophenol, o-amidobenzaldehyde, o-phthalic acid, o-oxycinnamic acid, etc.).

There are also crystallographic grounds favoring the idea that the meta-compounds stand between those of the ortho- and para-series (*Zeitschrift f. Kryst.*, 1879, 171; B. 18, R. 148).

The benzene hexagon not only expresses all the relations of isomerism of the benzene derivatives, but also abundantly illustrates their chemical and physical deportment.

Isomerism of the Benzene Polysubstitution Products.—If three or more hydrogen atoms of benzene be replaced, two cases arise: the substituting groups are like or unlike. In the first instance three isomerides of the tri-derivatives—*e. g.*, $C_6H_3(CH_3)_3$—are possible, and they occupy the positions:

(1, 2, 3) (1, 2, 4) and (1, 3, 5).

We call them *adjacent* (1, 2, 3) or (*v*) = vicinal, *unsymmetrical* (1, 2, 4) or (*as*) = asymmetrical, and *symmetrical* (1, 3, 5) or (*s*) tri-derivatives.

Three isomeric structural cases exist likewise for the tetra-derivatives, with four similar groups, $C_6H_2X_4$ (analogous to the di-derivatives):

(1, 2, 3, 4)	(1, 2, 4, 5)	(1, 2, 3, 5)
Adjacent	Symmetrical	Unsymmetrical.

Only one modification is possible when there are five and six similar groups; thus there exists but one pentachlorbenzene, C_6HCl_5, and but one hexachloride, C_6Cl_6.

When the substituting groups are unlike, the number of possible isomerides is far greater; they can easily be derived from the hexagon scheme. Thus, six isomeric modifications correspond to the formula of dinitrobenzoic acid, $C_6H_3(NO_2)_2 \cdot CO_2H$:

(1, 2, 3) (1, 2, 4) (1, 2, 5) (1, 2, 6) (1, 3, 4) (1, 3, 5);

here the carboxyl group occupies position 1.

The constitution of the polysubstitution products of benzene is deduced from their genetic relations to the diderivatives of benzene of known constitution.

See v. Meyer, B. **29**, 2564, etc., upon the deportment of polyalkylic benzene derivatives when the acetyl group is introduced by means of acetyl chloride and aluminium chloride, as well as for the conclusions to be drawn from the same in regard to the position of the substituents.

CONSTITUTION OF THE BENZENE NUCLEUS.

In Kekulé's formula, proposed in 1865, the six carbon atoms are attached to one another by alternating single and double bonds, forming a closed ring (p. 30). This,

assumption gives a rather comprehensive view of the entire behavior of the benzene derivatives:

1. It illustrates in the clearest manner possible the methods which have been employed in the synthesis of benzene derivatives (p. 41), benzene condensations, naphthalene, phenanthrene, etc. This has all been verified by the most recent syntheses (that of α-naphthol from phenylisocrotonic acid, etc.). Compare also B. **24**, 3117.

2. It is in complete harmony with the decomposition reactions of the benzene nucleus (p. 44).

3. It gives a simple explanation of the fact that only ortho-derivatives (because their side-chains are adjacent) are capable of forming anhydrides, and explains many derivatives due to ortho-condensations. The accepted benzene formula is made quite evident from the manner in which the quinoline ring is formed (Marckwald, A. **280**, 1).

4. The assumption of three double unions offers the simplest explanation (without new theories) for the power of benzene derivatives to yield additive products (p. 18). True, this addition does not occur as readily with the normal benzene compounds as it does with the methane compounds, in which there exist ethylene unions; however, aliphatic olefine derivatives also show gradual differences in this particular (see allyl alcohol, 1, p. 130). Consult v. Baeyer, A. **269**, 181, upon the assumption of para-additions in benzene.

5. Various physical properties argue for the presence of double unions, like those of ethylene, in benzene. Thus, the specific refractive powers indicate the presence of three ethylene unions, $CH=CH$, in benzene compounds, and five in naphthalene (Brühl, B. **27**, 1065). Compare Nasini, B. **23**, R. 276. The specific volumes of the benzene derivatives appear to support the idea of three double unions (1, p. 60).

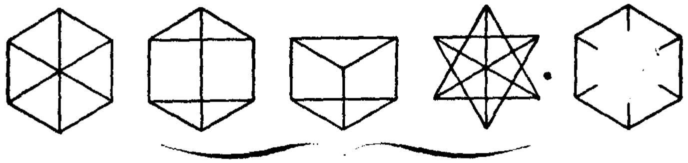
Kekulé's formula for benzene does not fully express the entire symmetry of the benzene nucleus. It would make the ortho derivatives (1, 2) and (1, 6) different, and allow of four different diderivatives, unless we admit Kekulé's idea of the oscillations of the adjacent carbon atoms (A. **162**, 86; B. **5**, 463; A. **279**, 195).

Perhaps in the formation of an ortho-diderivative there is a displacement of the double union if the substituting groups attach themselves to two singly-linked carbon atoms of the ring, so that that derivative will always be produced in which the substituting groups are joined to doubly-linked carbon atoms. The easier, more complete oxidation of the o-diderivatives, as compared with the corresponding m- and p-diderivatives, harmonizes with this conception.

It cannot be denied that the insufficiency of the Kekulé benzene formula is observable when predicting the existence of two instead of one modification of an ortho-disubstitution product. It may also be remarked that the many analogies predominating between the ortho- and meta-derivatives, as compared with the para-bodies, are not fully expressed by this formula. However, this formula, of all benzene formulas, is given the preference in this book, because it allows of a most complete view of the aromatic and aliphatic compounds.

Attention is also directed to other benzene formulas: The *diagonal formula* of Claus (A), the *prism formula* of Ladenburg (B_1, B_2, B_3), and the *central formula* of Armstrong and v. Baeyer (C):

A B_1 B_2 B_3 C



Claus: Diagonal formula — *Ladenburg*: Prism formula — *Armstrong-Baeyer*: Central formula.

Formulas A and B do not regard double unions as being present in the normal benzene nucleus. The existence of nine single linkages was thought to have been definitely

proved by the specific volumes of the benzene compounds, and especially by their heats of combustion (Theorie der Bildungswärme von J. Thomsen, B. **13**, 1808; **14**, 2944). According to the most recent researches, the specific volumes argue strongly for the presence of three divalent unions in the benzene nucleus, while the conclusions drawn from the heat of combustion are, in the opinion of Brühl, unfounded (J. pr. Chemie [2], **49**, 201).

Ladenburg's *prism formula* fully accounts for all the static relations of benzene, and explains its isomeric derivatives. It, however, ignores all the double unions, which are proved by the partially reduced benzene nuclei of the di- and tetra-hydro-additive products. It establishes a spacial orientation of the four affinities of the carbon atoms, which is without analogy in the paraffin series, and, in the opinion of its author, leaves to the formula of Kekulé the first place in explaining the various modes of formation and the decompositions of the benzene compounds (B. **23**, 1010).

The *diagonal formula* of A. Claus, with its hexagonal ring and its diagonal or central linkages, explains all the isomeric relations of the derivatives of benzene fully as well as the hexagon formula. It has the advantage that it permits of the formation of either para- or ortho-additive products, because it grants the double carbon-linkages in both the di- and tetra-hydro-benzenes (B. **20**, 1422; J. pr. Ch. [2], **49**, 505). But it also presents an orientation of the four carbon affinities that is without analogy, and introduces a peculiar central valence, differing from that of the two ring valences.

Baeyer has very recently introduced a *central formula*, which is very similar to the diagonal formula, but, unlike the latter, does not admit the presence of central linkages. It does not attempt to account for the state or condition of the fourth valence of carbon, but maintains merely that it exerts a pressure directed toward the center. It thus reverts to the hexagonal formula of benzene (Kekulé), which makes no attempt to explain the manner in which the fourth valences are combined (B. **23**, 1272; **24**, 2689; A. **269**, 145; B. **24**, R. 728).

Certain constitutional formulas proposed for benzene—*e. g.*, the octahedral formula of Thomsen (B. **19**, 2944) and the very noteworthy benzene model of Sacchse (B. **21**, 2530; Z. f. phys. Ch. **11**, 214; **23**, 2062)—are based on stereo-chemical considerations. The Ch. Ztg. (1894) **18**, 155, contains a list of benzene formulas.

BENZENE RING-FORMATIONS.

The nucleus-synthetic reactions of aliphatic bodies, in which the benzene ring is produced, are not especially numerous, but they are, however, very important, because they connect the aliphatic with the aromatic derivatives containing one nucleus. On this account they will be brought together before the individual classes of compounds are discussed, and will be arranged in the order according to which the starting-out bodies under the aliphatic compounds have been discussed:

1. CH_4, *Methane*, conducted through a tube heated to redness, yields *benzene*.

2. $3CH\equiv CH$, *Acetylene*, polymerizes at a red heat to *benzene* (1, p. 96).

3*a*. $3CH\equiv C.CH_3$, *Allylene*, is polymerized by concentrated sulphuric acid to [1,3,5]-*trimethylbenzene* or mesitylene (1, p. 98).

3*b*. $3CH_3.C\equiv C.CH_3$, *Crotonylene*, polymerizes to *hexamethylbenzene*.

4. CCl_4, *Perchlormethane*, and $CCl_2{=}CCl_2$, *perchlorethylene*, yield *perchlorbenzene* when they are conducted through a tube heated to redness; compare *perbrombenzene*.

5. $3CH\equiv CBr$, *Monobromacetylene*, polymerizes to [1,3,5]-tribrombenzene (1, p. 106).

6. $C_6H_{13}I$, *Hexyl iodide*, when acted upon by iodine chloride, yields *hexachlorbenzene*; with bromine the product is *hexabrombenzene*.

7*a*. $(CH_3)_2CH . CH_2 . CH : CH . C(CH_3) : CH . CHO$, ***Geranial***, or ***citral***, yields [1,4]-*isopropyltoluene* or *cymene*, when it is acted upon with potassium bisulphate.

7*b*. $CH_3 . CH_2 . CH : C(CH_3) . CH : CH . CO . CH_3$, from methyl ethyl acroleïn and acetone, yields *pseudo-cumene*.

7*c*. $(C_3H_7) . CH_2 . CH : C(C_3H_7) . CH : CH . CO . CH_3$, from two molecules of isovaleraldehyde and one molecule of acetone, yields *di-isopropyltoluene* (B. **28**, R. 608).

8*a*. $3CH_3 . CO . CH_3$, *Acetone*, under the influence of sulphuric acid, yields [1,3,5]-*trimethylbenzene* or *mesitylene* (1, p. 214).

8*b*. $3CH_3 . CO . CH_2 . CH_3$, *Methylethylketone*, changes to [1,3,5]-*triethylbenzene*.

8*c*. $3CH_3 . CO . CH_2 . CH_2 . CH_3$, *Methyl-n-propylketone*, yields [1,3,5]-*tri-n-propylbenzene*.

9. $6CO$, *Carbon monoxide*, combines at high temperatures with potassium to form *potassium hexaoxybenzene* (1, p. 236).

10. $3CH_3 . CH_2 . CH_2 . COCl$, *Butyryl chloride*, is condensed by Al_2Cl_6 to *triethylphloroglucin*.

11. $3CH{\equiv}C . CO_2H$, *Propiolic acid*, polymerizes in sunlight to [1,3,5]-*benzenetricarboxylic acid* or *trimesic acid*.

12. $3NO_2CH(CHO)_2$, *Nitromalonic aldehyde*, passes into sym. *trinitrobenzene*, when its sodium salt is decomposed.

13. $NO_2 . CH(CHO)_2$, *Nitromalonic aldehyde*, and $CH_3 . CO . CH_3$, *acetone*, yield *p-nitrophenol* (B. **28**, 2597).

14. $3CH_3 . CO . CH = CH . OH$, *Oxymethylene acetone*, or *formyl acetone*, condenses very easily to [1,3,5]-*triacetylbenzene*, $C_6H_3(COCH_3)_3$ (1, p. 319).

15*a*. $2CH_3 . CO . CO . CH_3$, *Diacetyl*, is condensed by alkalies to *p-xyloquinone* or [2,5]-*dimethylquinone*.

15*b*. $2CH_3 . CO . CO . CH_2 . CH_3$, *Acetylpropionyl*, yields *duroquinone* or *tetramethylquinone*.

16. $3CH(OH){=}CH . CO_2 . C_2H_5$, *Oxymethylene acetic ester* or *formylacetic ester*, and its dimolecular condensation product, *coumalic acid*, condense quite readily to esters of [1,3,5]-*benzene tricarboxylic acid* or *trimesic acid*.

17*a*. $2CH_3 . CO . CO_2H$, *Pyroracemic acid*, and $CH_3 . CHO$, *acetaldehyde*, when heated with baryta water, condense to [1,3,5]-*methylisophthalic acid* or *uvitic acid*.

17*b*. $2CH_3 . CO . CO_2H$, *Pyroracemic acid*, and $CH_3 . CH_2 . CHO$, *propionic aldehyde*, yield [1,3,5]-*ethylisophthalic acid*.

18. $2CH_3 . CO . CHNa . CO_2 . C_2H_5$, *Sodium acetoacetic ester*, and $CHCl_3$, *chloroform*, rearrange themselves to oxyuvitic ester or oxymethyl-isophthalic ester.

19. $CH_3 . C : CH . CO . CH . CO . CH_3$ (ring closed: O — CO), *Dehydracetic acid*, yields *orcinol* or 3,5-*dioxytoluene*.

20. $2CH_3 . CO . CH_2 . CO . CO_2 . C_2H_5$, *Acetonoxalic ester*, condenses to *oxytoluic ester*.

It is very doubtful whether a synthesis occurs in the production of *mellitic acid* or *benzene hexacarboxylic acid*, $C_6(CO_2H)_6$, by the oxidation of coal or graphite. It is more probable that this reaction must be regarded as a transformation or rearrangement of a carbon molecule consisting of twelve carbon atoms.

Reviewing the aliphatic bodies which are converted into benzene derivatives by nucleus-synthetic reactions, it will be discovered that

1. Certain saturated bodies like methane (1) and tetrachlormethane (4) yield the benzene ring under the influence of heat,—by *pyrocondensation*. Many benzene derivatives, like benzene, the methyl benzenes, the simple amido- and oxybenzenes, are distinguished by their remarkable stability at high temperatures (see coal tar, p. 48).

2. Perchlorbenzene has been observed in the *exhaustive chlorination* of many aliphatic substances. Hexyl iodide (6) is converted into perchlor- and perbrom-benzene with especial ease.

3. A great number of aliphatic acetylene derivatives containing a trebly-linked pair of carbon atoms *polymerize*, and by the union of three similar molecules form benzene derivatives. The polymerization of acetylene to benzene (2) occurs with the greatest difficulty. Bromacetylene (5) polymerizes much more readily. Allylene (3*a*) and crotonylene (3*b*) require sulphuric acid, and propiolic acid (11) sunlight in order to bring about *aromatic polymerization*.

The other aliphatic compounds capable of condensing to aromatic substances, which, in other words, manifest *aromatic condensation*, contain carbon and oxygen linked doubly to each other. Many of them are ketones; others contain the oxymethylene group.

4. The production of potassium hexaoxybenzene from carbon monoxide and potassium (9) is based upon a direct *addition-reaction*. The following are *hydrolytic condensations*:

5. The ring-formation in the transition of citral or geranial and other high molecular keto-olefines into cymene, pseudocumene, and isopropyltoluene (7*a*, *b*, *c*), as well as the condensation of dehydracetic acid to orcinol (19). This proceeds with the exit of carbon dioxide.

6. The condensation of acetone, methyl-ethyl- and methyl-n-propylketone to [1,3,5]-trialkylic benzenes (8*a*, 8*b*, 8*c*). A similar reaction is that of butyryl chloride, which splits off hydrochloric acid three times and condenses to triethylphloroglucin (10).

7. The condensation of pyroracemic acid and aldehydes to [1,3,5]-alkylic isophthalic acids (17*a*, 17*b*).

8. The condensations of nitromalonic aldehyde and of the oxymethylene compounds (12, 13, 14, 16) are related to the condensations considered under 6 and 7.

9. Two aliphatic molecules take part in the hydrolytic condensation of α-diketones—*e. g.*, diacetyl and acetylpropionyl to p-xylo- and duroquinone (15*a*, 15*b*); (10) acetonoxalic acid to oxytoluic acid (20).

11. Three aliphatic molecules (18) participate in the condensation of chloroform and sodium acetoacetic ester.

Various other reactions attach themselves to those indicated in the preceding paragraphs, which lead to the formation of the benzene ring. They result in the production of hydroaromatic compounds, bearing,

an intimate kinship to the derivatives of benzene. Some of them are:

1. Sodium malonic ester condenses to phloroglucin tricarboxylic ester, sodium acetone dicarboxylic ester to dioxyphenylaceto-dicarboxylic ester, while triketohexamethylene dicarboxylic ester is formed from acetone dicarboxylic ester and malonic ester (B. **29**, R. 1117). All these condensation products are probably hexahydrobenzene derivatives.

2. Succinic ester is condensed by metallic sodium to succinylosuccinic ester.

3. $\alpha\gamma$-Diacetoglutaric ester changes readily to 3-methyl-Δ_2-ketohexa methylene. Condensations of δ diketo bodies, such as the preceding, are rather numerous. Thus, γ-acetobutyric ester, $CH_3.CO.CH_2.CH_2.$-$CH_2.COOC_2H_5$, and sodium ethylate yield dihydroresorcinol, which conversely breaks down into γ-acetobutyric acid (compare decompositions of the benzene ring).

Other methods showing the synthesis of hydroaromatic compounds have already been given (pp. 20, 21).

DECOMPOSITIONS OF THE BENZENE RING.

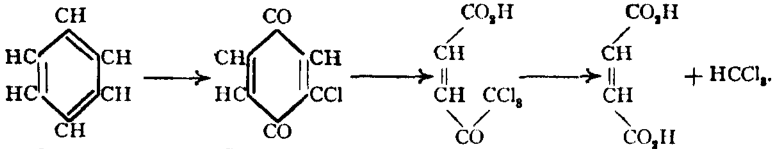
The benzene derivatives in general are characterized by the stability of the benzene ring. To break the latter down the proper benzene bodies are acted upon by reagents which open up the double union in part or entirely. Hence, the decomposition is invariably preceded by the formation of hydroaromatic intermediate products, which usually cannot be isolated. Often decomposition products result, which still contain the six carbon atoms in the molecule as an open chain, but usually they are fragments of the decomposition, and in some instances they are pentacarbocyclic derivatives formed from hexacarbocyclic α-diketones.

The phenols, amidophenols, quinones, oxyquinones, and phenol carboxylic acids are most suitable for the ring-decomposition.

1. Decomposition by Moderated Oxidation.—Although energetic oxidation decomposes the benzene nucleus of the aromatic substances referred to in such a manner that bodies containing two carbon atoms result,—*e.g.*, carbon dioxide, formic acid, and oxalic acid,—yet it has been possible, by means of nitrous acid, to oxidize pyrocatechol or [1,2]-dioxybenzene, $C_6H_4[1,2](OH)_2$, and protocatechuic acid or [3,4]-dioxybenzoic acid, $CO_2H[1]C_6H_3[3,4](OH)_2$, to dioxytartaric acid (Kekulé).

Phenol, C_6H_5OH, has been converted by dilute potassium permanganate into mesotartaric acid (Döbner).

2. Decomposition by Simultaneous Chlorination and Oxidation.—When benzene is treated with potassium chlorate and sulphuric acid, trichlorphenomalic acid or β-trichloracetoacrylic acid (1, p. 382) is produced (chlorquinone is an intermediate product), which breaks down, under the influence of baryta water, into chloroform and maleïc acid (Kekulé and Strecker):



Benzene — Chlorquinone — Trichlorphenomalic Acid, or β-Trichloraceto-acrylic Acid — Maleïc Acid.

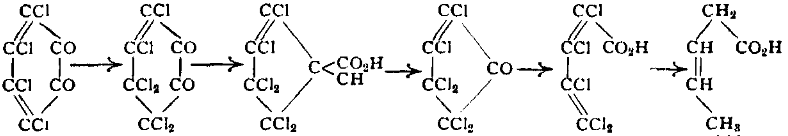
Potassium chlorate and hydrochloric acid change phenol, salicylic acid, or o-oxybenzoic acid, $CO_2H[1]C_6H_4[2]OH$, and gallic acid, $CO_2H[1]C_6H_2[2,3,4](OH)_3$, into trichlorpyroracemic acid or isotrichlorglyceric acid, $CCl_3C(OH)_2CO_2H$ (see I, 370).

Bleaching lime converts picric acid or [1OH,2,4,6]-trinitrophenol into chlorpicrin (vol. 1), while bromine and lime-water change it to brompicrin (vol. 1).

Zincke has given an interesting method for the decomposition of the benzene nucleus. It consists in preparing chlorinated R-hexene- and R-hexylene ketones from suitable aromatic bodies, and then decomposing the first.

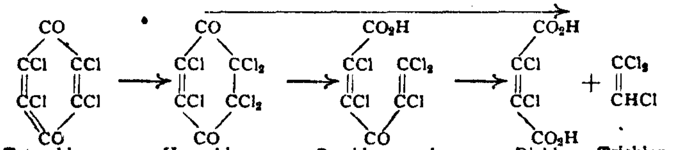
Four examples may be given. The first three attach themselves to the three dioxybenzenes and the fourth to [1,3,5]-trioxybenzene or phloroglucin.

1. Chlorine converts pyrocatechol or o-dioxybenzene first into tetrachlororthoquinone, and this into hexachlor-o-diketo-R-hexene. The latter compound, when digested with water, sustains a rearrangement into hexachlor-R penteneoxycarboxylic acid, which chromic acid oxidizes to hexachlorketo-R-pentene. Caustic soda resolves the R-pentene ketone into perchlorvinylacrylic acid, which becomes ethidenepropionic acid upon reduction (B. 27, 3364):



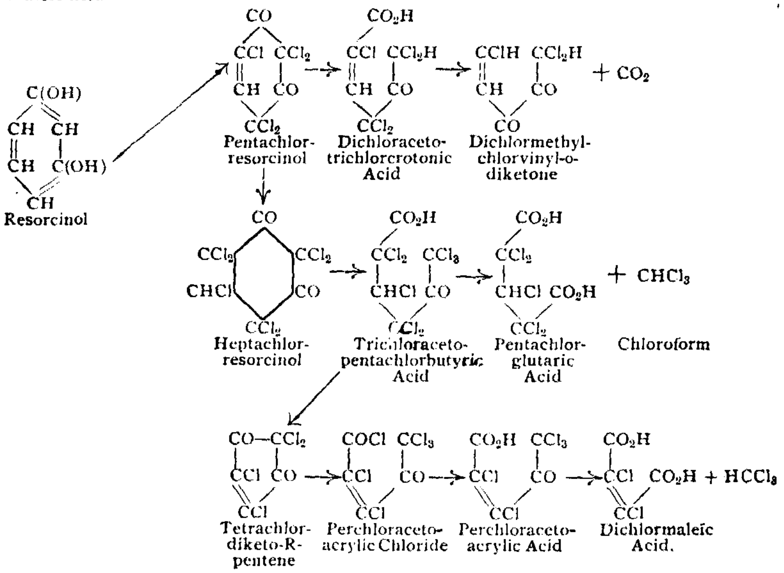
Tetra-chlor-o-quinone — Hexachlor-o-diketo-R-hexene — Hexachlor-R-penteneoxy-carboxylic Acid — Hexachlor-keto-R-pentene — Perchlor-vinyl-acrylic Acid — Ethidene-propionic Acid.

2. The decomposition of *hydroquinone* proceeds more simply. Tetrachlorparaquinone is readily formed by the action of chlorine upon hydroquinone or quinone, as well as by the action of potassium chlorate and hydrochloric acid upon phenol. The further addition of chlorine leads to hexachlorparadiketo-R-hexene, which is converted by alcoholic potash into perchloracroylacrylic acid. The latter, and also hexachlorparadiketo-R-hexene itself, are decomposed by aqueous caustic soda into dichlormaleïc acid, trichlorethylene, and hydrochloric acid (A. 267, 1):

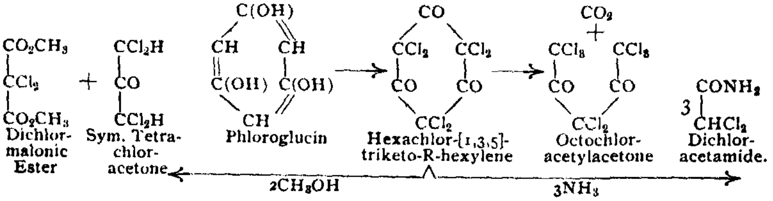


Tetrachlor-p-quinone — Hexachlor-p-diketo-R-hexene — Perchloracroyl-acrylic Acid — Dichlor-maleïc Acid — Trichlor-ethylene.

3. Chlorine converts *resorcinol*, in glacial acetic solution, into pentachlorresorcinol, and this into heptachlorresorcinol. Both m-diketochlorides are decomposed by cold water; the pentachlor-derivative yields dichloracetotrichlorcrotonic acid, while the hepta- body yields trichloracetopentachlorbutyric acid under the influence of chlorine and water. When dichloracetotrichlorcrotonic acid is boiled with water it becomes di-chlormethylchlorvinyl-o-diketone. Trichloracetopentachlorbutyric acid is decomposed by alkalies, the same as trichloracetoacrylic acid, into chloroform and pentachlorglutaric acid. If, however, it be treated with boiling water, it changes to tetrachlordiketo-R-pentene, which chlorine converts into the chloride of perchloracetoacrylic acid. Water changes the chloride to the acid, which alkalies decompose into chloroform and dichlor-maleïc acid:



4. Phloroglucin, or [1,3,5]-trioxybenzene, behaves just like resorcinol. Chlorine converts it into hexachlor-[1,3,5]-triketo-R-hexylene. Water and chlorine decompose the triketone into octochloracetylacetone; methyl alcohol changes it to the dimethyl ester of dichlormalonic acid, and sym. tetrachloracetone; while with ammonia it yields three molecules of dichloracetamide (B. 23, 1706):

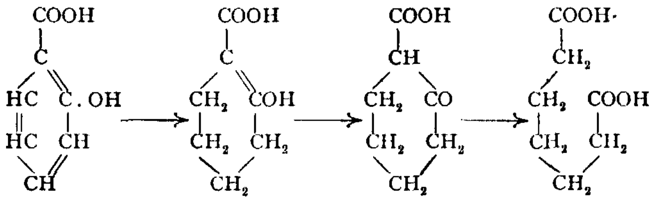


In the four preceding examples the decomposition occurs between a CO-group and a CCl_2-group of a ketochloride. Zincke first elaborated these reactions in the naphthalene series, and used them to effect the decomposition of the one naphthalene nucleus, and for the transformation of naphthalene into indene derivatives. Later he extended them

to the phenols and other aromatic bodies which have been mentioned. Hantzsch, in like manner, effected the decomposition of phenol in an alkaline solution, and changed it to cyclopentene compounds (B. **22**, 1238).

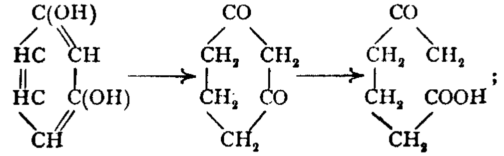
3. Decomposition by Reduction in Alkaline Solution.—This decomposition is shown by—

I. The o-phenolcarboxylic acids when they are reduced by metallic sodium in amyl alcoholic solution. It is very probable that the intermediate products of the reduction are tetrahydroacids and their products of rearrangement—the hydroaromatic o-ketone carboxylic acids. The latter absorb water and become pimelic acids. Salicylic acid is converted almost quantitatively into n-pimelic acid, while o-, m-, and p-cresotinic acids yield the three isomeric methyl pimelic acids (Einhorn and Willstätter, B. **28**, R. 744):



This reaction has been carried out with equal success with the naphthalene-o-oxycarboxylic acids (see decompositions of the naphthalene ring).

II. Reduction changes resorcinol into dihydroresorcinol, which is converted into n-glutaric acid by oxidation with potassium permanganate (Merling, A. **278**, 32). If dihydroresorcinol be heated for several hours with a concentrated baryta solution to 150–160°, it takes up water and decomposes into γ-acetobutyric acid (Vorländer, B. **28**, 2348):



This reaction can be made retrogressive (compare p. 44).

I. BENZENE HYDROCARBONS CONTAINING A SINGLE NUCLEUS.

Benzene, *Phene,* C_6H_6, melting at + 5.4° and boiling at 80.4° (760 mm.), is the parent hydrocarbon of the aromatic compounds. It is produced in the dry distillation of coal, and is accordingly present in coal tar, accompanied by thiophene, C_4H_4S (a body which may be readily confounded with it in physical properties), and numerous other deriva-

tives. Pure benzene is obtained by heating benzoic acid or other benzene polycarboxylic acids with lime. It is prepared synthetically by heating acetylene to high temperatures (Berthelot, 1870).

Benzene is obtained from coal tar by fractional distillation. The presence of thiophene in it is readily determined by the indophenine or phenanthraquinone reaction (see thiophene). The thiophene can be removed from the benzene by shaking the latter with concentrated sulphuric acid, or by acting upon it with aluminium chloride (B. 29, R. 1000, 1152). It is finally purified by surrounding it with a freezing mixture, and the crystalline benzene is pressed out in the cold.

History (B. 23, 1271).—Faraday (1825) discovered benzene in an oil obtained by the compression of illuminating gas. In 1834 Mitscherlich obtained it by distilling benzoic acid with lime, and in 1845 Hofmann found it in coal tar.

Properties.—Benzene is a mobile, ethereal-smelling liquid, of specific gravity 0.899 at 0° (0.8799 at 20°). It burns with a luminous flame, mixes with absolute alcohol and ether, and readily dissolves resins, fats, and many carbon compounds, some of which crystallize out in combination with the benzene (see triphenylmethane). Sulphur, iodine, and phosphorus are also soluble in benzene.

Deportment and Transformations.—(1) When benzene is conducted through tubes heated to redness it loses hydrogen and changes partly into diphenyl, $C_6H_5 . C_6H_5$, diphenyl benzenes, $C_6H_4(C_6H_5)_2$, etc., and in part into acetylene. (2) If benzene be acted upon with manganese dioxide and sulphuric acid some benzoic acid is produced, due evidently to the diphenyl formed at first (A. 221, 234), and also o-phthalic acid. The benzene is, however, quite stable in the presence of oxidants; but when potassium chlorate and sulphuric acid act upon it, it is torn asunder and becomes trichlorphenomalic acid or β-trichloracetoacrylic acid (p. 45). Benzene exposed for a long period to the action of ozone changes to a white, amorphous mass—*ozobenzene*. This is a very explosive body. It has the formula $C_6H_6O_6$. Water slowly decomposes it (B. 28, R. 540, 1054). (3) Hydriodic acid reduces it to [cyclohexane] or hexahydrobenzene (see this) (A. 278, 88). (4) Chlorine and bromine not only add themselves to benzene, but also replace its hydrogen (p. 58). (5) Nitric acid converts it into nitrobenzene, $C_6H_5NO_2$. (6) Sulphuric acid changes it to benzene sulphonic acid, $C_6H_5SO_3H$. These last two compounds are made upon a technical scale. Alkyl residues can be introduced into benzene by the action of Al_2Cl_6 and alkylogens (see formation (4) of benzene hydrocarbons, p. 50). (7) Benzene and aldehydes are condensed by sulphuric acid to higher aromatic hydrocarbons (see diphenylmethane and diphenylethane).

COAL TAR.

Not only benzene, but also numerous methyl benzenes and many more highly condensed aromatic hydrocarbons, like *naphthalene*, $C_{10}H_8$, *acenaphthene*, $C_{12}H_{10}$, *fluorene*, $C_{13}H_{10}$, *anthracene* and *phenanthrene*, $C_{14}H_{10}$, *fluoranthene*, $C_{15}H_{10}$, *pyrene*, $C_{16}H_{10}$, *chrysene*, $C_{18}H_{12}$, etc., are obtained by the dry distillation of coal. They are present in coal tar, which is produced in great quantities in the manufacture of illuminating gas and in the coke industry. In addition to gas and tar, which are products of coal distillation, mention must also be made of the ammonia water. These are the volatile products. Coke remains in the retorts. It is a better fuel than coal; it is richer in carbon.

The rapid, brilliant development of the chemistry of the benzene de-

rivatives is largely due to the fact that the aromatic parent hydrocarbons are so largely present in coal tar, and are accessible in large amounts through various technical industries. The very nature of the paraffins renders them unsuitable for the preparation of the aliphatic bodies, whereas the benzene hydrocarbons, because of the readiness with which they enter into all kinds of reactions, constitute not only the systematic, but also the practical foundation for the upbuilding of the chemistry of the aromatic derivatives. Coal tar, which contains these hydrocarbons, is an inexhaustible source for the preparation of numerous benzene derivatives, not a few of which have found extensive application as dyes or medicines.

The Working of Coal Tar for Aromatic Hydrocarbons.—The tar contains not only aromatic hydrocarbons, but also paraffins, thiophene, methylated thiophenes, phenols, pyridine bases, and other derivatives. It is first distilled and then separated into three or four fractions:

1. *Light Oil* (3–5 per cent.), specifically lighter than water and boiling up to 150°.
2. *Middle Oil* (8–10 per cent.), having about the same specific gravity as water and boiling from 150–210°.
3. *Heavy Oil* (8–10 per cent.), heavier than water and boiling at 210–270°.
4. *Green Oil* or *Anthracene Oil* (16–20 per cent.), colored green, and boiling from 270–400°.
5. Residue: *pitch.*

It is only the light oil which is of value when the aromatic hydrocarbons are under consideration. It is freed from resins, olefines, pyridine bases, etc., by washing with sulphuric acid, and from phenols by treating it with caustic soda. After this it is subjected to careful, fractional distillation in a column apparatus like that employed in the purification of alcohol (I, p. 123).

Besides benzene, coal tar contains *toluene* or methyl benzene, the three isomeric *xylenes* or dimethyl benzenes, ethyl benzene, *vinyl benzene* or *styrene*, the three isomeric trimethyl benzenes; mesitylene, *pseudocumene*, hemimellithene and durene or tetramethyl benzene. Aromatic hydrocarbons also occur abundantly in the tar from peat, in small amount in the tar from wood, in that from bituminous shales, and in petroleum.

To properly understand the formation of the aromatic hydrocarbons by the dry distillation of coal we should take into consideration that they are produced with hydrogen evolution on passing simple, fatty bodies like methane, alcohol, ether, etc., through tubes heated to redness (B. 29, 2691). Such reactions are termed *pyrogenic syntheses* or *pyrocondensations*, in which acetylene and allylene particularly play an important rôle. Just as acetylene yields benzene, so acetylene and allylene form toluene, and benzene and acetylene yield naphthalene, etc. (A. 139, 281; B. 10, 853; 11, 1213; 18, 3032; 19, 2513; 20, 660). The glowing sides of the retort with which the volatile products resulting in the heating of coal come in contact give every opportunity for such pyrocondensations. However, the nature of the starting-substances should really be carefully considered (B. 28, 488).

ALKYL BENZENES, C_nH_{2n-6}.

The *nucleus-synthetic reactions* (1, 85) stand first among the general methods of formation used in connection with the alkyl benzenes (it has been indicated in preceding paragraphs that the methyl benzenes occur in coal tar).

1. It has been repeatedly stated that various symmetric trialkylic benzenes have been obtained by the polymerization of alkyl acetylenes with sulphuric acid, similarly to the polymerization of acetylene to benzene (p. 41):

Allylene, $3CH_3 . C \equiv CH \xrightarrow{SO_4H_2} C_6H_3[1,3,5](CH_3)_3$, Mesitylene.

Ketones, such as acetone, ethylmethyl ketone, etc., can be treated with sulphuric acid, instead of the alkyl acetylenes (p. 42).

2. The reaction of Fittig, discovered in 1864, is more generally used. It consists of the action of sodium upon a mixture of brominated benzenes, and the bromides or the iodides of the alkyls in ethereal solution (A. **129**, 369; **131**, 303; B. **21**, 3185):

$$C_6H_5Br + CH_3I + 2Na = C_6H_5 . CH_3 + NaI + NaBr,$$

$$C_6H_4Br . C_2H_5 + C_2H_5I + 2Na = C_6H_4\begin{cases}C_2H_5\\C_2H_5\end{cases} + NaI + NaBr.$$

This reaction is a valuable generalization of the synthesis applied by Würtz to the paraffins, which consisted in acting on the alkylogens with sodium (1, 84). A few drops of acetic ether sometimes accelerate the reaction, which proceeds the more smoothly the greater the molecular weight of the alkyl iodide.

3. The synthesis of isopropyl benzene from benzal chloride and zinc methide (B. **13**, 45), and that of the one amyl benzene from benzal chloride and zinc ethide, corresponds to that of tetramethyl methane from acetone chloride and zinc methide (1, 85);

$$C_6H_5CHCl_2 + Zn(C_2H_5)_2 = C_6H_5CH(C_2H_5)_2 + ZnCl_2.$$

4. The so-called aluminium chloride synthesis discovered by Friedel and Crafts in 1877, although restricted to the aromatic series, is there very generally applicable. It consists in the action of alkylogens upon benzene hydrocarbons in the presence of aluminium chloride.

Zinc chloride and ferric chloride act similarly. It is very probable that metallo-organic bodies—*e.g.*, $C_6H_5 . Al_2Cl_5$—are formed at first. These then react with the alkylogens. No difficulty is experienced in replacing all the hydrogen atoms of benzene by methyl or ethyl groups (B. **14**, 2624; **16**, 1745). Sometimes carbon disulphide acts favorably as a diluent (A. **235**, 207; B. **29**, 2884):

$$CH_3Cl + C_6H_6 \xrightarrow{Al_2Cl_6} HCl + C_6H_5CH_3$$

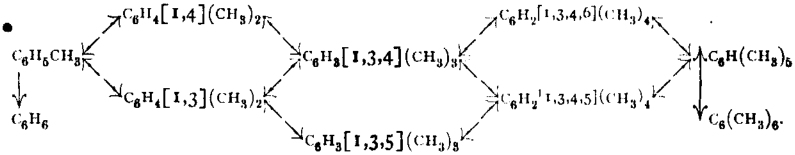
$$2CH_3Cl + C_6H_6 \xrightarrow{Al_2Cl_6} 2HCl + C_6H_4(CH_3)_2$$

$$6CH_3Cl + C_6H_6 \xrightarrow{Al_2Cl_6} 6HCl + C_6(CH_3)_6.$$

Various haloid compounds—*e.g.*, chloroform (see triphenylmethane)—and the acid radicals (see benzophenone and acetophenone) react similarly with benzene.

Decomposition Reactions.—5. It is rather singular that aluminium chloride lends itself as well to the breaking-down of alkyl benzenes as to their synthesis.

Thus, aluminium chloride acting alone, or more especially when HCl is conducted into polyalkylic benzenes mixed with aluminium chloride, causes the side-chains to split off in the form of alkyl chlorides (A. **235**, 177). Under proper experimental conditions it is possible, with the aid of aluminium chloride, to remove the side-chains from one molecule of an hydrocarbon into another molecule of the same hydrocarbon. In so doing the aluminium chloride seems to prefer certain very definite positions of the alkyl groups both in the synthesis and in the decomposition. This is illustrated in the following diagram (Anschütz and Immendorff, B. **18**, 657):



6. Concentrated sulphuric acid acts in the same decomposing way, building up new bodies at the same time (see durene, p. 55).

7. Dry distillation of a mixture of aromatic acids with lime or soda-lime (1, p. 81); iron filings are introduced to accelerate the conduction of heat. All the carboxyl groups are split off in the reaction and the original hydrocarbons set free:

Benzoic Acid, ...	$C_6H_5.CO_2H \longrightarrow CO_2 + C_6H_6$ . . .	Benzene.
Toluic Acids, . .	$CH_3.C_6H_4.CO_2H \longrightarrow CO_2 + C_6H_5.CH_3$	Toluene.
Phthalic Acids, . . .	$C_6H_4(CO_2H)_2 \longrightarrow 2CO_2 + C_6H_6$ . . .	Benzene.

8, 9, and 10. *The replacement of inorganic residues in substitution products of the aromatic hydrocarbons by hydrogen.*

8. Treatment of diazo-bodies with alcohol or an alkaline solution of stannous oxide (B. **22**, 587). This reaction is of special value in the determination of questions of constitution. The diazo-bodies are obtained from amido-compounds, and these from nitro-derivatives, which result when nitric acid acts upon the hydrocarbons.

9. Treatment of sulpho-acids (see these) with superheated steam and sulphuric acid, concentrated hydrochloric acid or phosphoric acid at 180°.

10. Heating the oxygen derivatives—*e. g.*, phenols and ketones—with zinc dust (Baeyer, A. **140**, 295), or with hydriodic acid and phosphorus. It is remarkable that benzophenone, $C_6H_5.CO.C_6H_5$, for example, is readily reduced, while the opposite is true of diphenyl ether, $C_6H_5.O.C_6H_5$.

Properties.—The hydrocarbons of the benzene series are chiefly volatile liquids; some polymethylbenzenes—durene, penta- and hexamethylbenzene—are solids at ordinary temperatures. They possess a peculiar, not disagreeable odor, and are insoluble in water. They dissolve readily in alcohol and in ether. They are excellent solvents for many organic substances, which can be precipitated from solution by petroleum ether.

Deportment and Transformations.—(1) Reducing agents, particularly hydriodic acid, convert the alkyl benzenes, and also benzene itself, into

hydroaromatic hydrocarbons (p. 18). (2) The behavior of the alkyl benzenes under oxidation is very important.

Acids are produced (aromatic acids) by oxidizing their side-chains with nitric acid, a chromic acid mixture, potassium permanganate, or ferricyanide of potassium.

The number and position of the resulting CO_2H groups with reference to each other afford evidence as to the number and position of the alcohol radicals contained in the oxidized hydrocarbon. When long side-chains are carefully oxidized, particularly with potassium permanganate, intermediate products can be obtained, since the oxidation occurs according to the rules which prevail with aliphatic compounds (compare aromatic acids).

(3) Chlorine and bromine replace the hydrogen of the benzene nucleus when they act upon it in the cold, whereas it is the hydrogen of the side-chains which is substituted in the heat (toluene, pp. 54, 61).

(4) Concentrated nitric acid produces nitro-bodies.

(5) Concentrated sulphuric acid, aided by heat, dissolves the alkyl benzenes with formation of sulphonic acids. The hydrocarbons can be recovered again from the latter (see method 9). This constitutes the basis of a method for the separation of the benzenes from the paraffins, as well as affords a means of obtaining the former in a state of purity.

(6) Chromyl chloride, CrO_2Cl_2, unites with the benzene homologues to form compounds which water converts into aromatic aldehydes and ketones (see these).

Isomerism.—*Toluene*, the first member of the series, is only known in one modification. More are not possible. The six hydrogen atoms of benzene are equal (p. 30).

Xylene, or *dimethyl benzene*, is a disubstitution product; therefore three isomerides are possible (p. 32):

o-Xylene, $C_6H_4\begin{cases}[1]\,CH_3\\ [2]\,CH_3\end{cases}$ m-Xylene, $C_6H_4\begin{cases}[1]\,CH_3\\ [3]\,CH_3\end{cases}$ p-Xylene, $C_6H_4\begin{cases}[1]\,CH_3\\ [4]\,CH_3\end{cases}$.

The three xylenes are known. *Ethyl benzene*, $C_6H_5C_2H_5$, is isomeric with them.

There are eight possible isomerides of the formula C_9H_{12}; all of them are known. They are—

1. Three trimethyl benzenes.
2. Three ethylmethyl benzenes.
3. Two propyl benzenes: n-propyl and isopropyl benzene.

The phenomena of isomerism are, therefore, influenced by the place or position, the number, the homology and isomerism of the alkyls, which have entered the benzene as substituents of the hydrogen.

Constitution.—Of all the syntheses of alkyl benzenes, the reaction of Fittig is most suitable for the deduction of conclusions in regard to constitution, because, so far as is known, intramolecular atomic rearrangements do not occur in it—that is, the alkyls assume the position previously held by the halogen atom. Further, the oxidation reaction is important in deciding upon the number and position of the side-chains (see above).

Name.	Formula.	M. P.	B. P.	Specific Gravity.
Toluene, ...	$C_6H_5.CH_3$ . . .	—	110.3°	0.8708 (13.1/4°)
Xylenes, Dimethyl Benzenes, .	$C_6H_4(CH_3)_2$ . . .			
o-Xylene, ...	. . . .	— 28°	142°	0.8932 (0°)
m-Xylene, **Isoxylene**, . .	. . . .	— 54°	139°	0.8812 (0°)
p-Xylene, ...	. . . .	+ 15°	138°	0.8801 (0°)
Ethyl Benzene, ...	$C_6H_5.CH_2.CH_3$.	—	134°	0.8832 (0°)
Trimethyl Benzenes, ...	$C_6H_3(CH_3)_3$ . . .			
[1,2,3]=Hemimellithene, .	. . . .	—	175°	—
[1,2,4]=**Pseudocumene**, .	. . . .	—	170°	—
[1,3,5]=**Mesitylene**, . .	. . . .	—	164.5°	0.8694 (9.8/4°)
Methylethyl Benzenes, . . .	$C_6H_4(CH_3)(C_2H_5)$.			
o- or [1,2]-, ...	. . . .	—	159°	0.8731 (16°)
m- or [1,3]-, ...	. . . .	—	159°	0.8690 (20°)
p- or [1,4]-, ...	. . . .	—	162°	0.8652 (21°)
n-Propyl Benzene, ...	$C_6H_5.CH_2.CH_2.CH_3$	—	158.5°	0.8810 (0°)
Isopropyl Benzene, **Cumene**,	$C_6H_5CH(CH_3)_2$.	—	153°	0.8798 (0°)
Tetramethyl Benzene, ...	$C_6H_2(CH_3)_4$ . . .			
[1,2,3,4]=Prehnitol, . . .	. . . .	—4°	204°	—
[1,2,3,5]=Isodurene, . .	. . . .	—	196°	0.8961 (0/4°)
[1,2,4,5]=Durene, ...	. . . .	79°	190°	—
Cymene, [1,4]-Methylisopropyl Benzene, ...	$C_6H_4(CH_3)(C_3H_7)$.	—	175°	0.8723 (0°)
Pentamethyl Benzene, ...	$C_6H(CH_3)_5$	53°	230°	—
Hexamethyl Benzene, ...	$C_6(CH_3)_6$	164°	264°	—
Pentaethyl Benzene, ...	$C_6H(C_2H_5)_5$ . . .	—	277°	0.8985 (19°)
Hexaethyl Benzene, ...	$C_6(C_2H_5)_6$	129°	298°	—

It is apparent from this table that the position isomerides of the same formula—that is, the three xylenes—have almost the same boiling point. In the case of the dimethyl benzenes the o-modification has the highest boiling point; then follows the meta-body, and finally the p-compound. However, the latter has the highest melting point. Durene of the tetramethyl benzenes is a solid at the ordinary temperature. This is also true of pentamethyl-, hexamethyl-, and hexaethyl-benzenes. The entrance of methyl into the side-chain raises the boiling point about 24°. See toluene, ethyl benzene, and n-propyl benzene.

Toluene, $C_6H_5CH_3$, so called because it is produced in the dry distillation of tolu balsam, occurs in coal tar, accompanied by thiotolene or methyl thiophene (see this). It is very valuable from a commercial standpoint. It is produced by the usual methods:

1. From brombenzene, methyl iodide, and sodium.
2. From benzene, methyl chloride, and aluminium chloride.
3. From the polymethyl benzenes and aluminium chloride.
4. By distillation of the three toluic acids and the methyl polycarboxylic acids with lime, etc.

Reduction changes toluene to *hexahydrotoluene*; dilute nitric acid and chromic acid oxidize it to benzoic acid; chromyl chloride, CrO_2Cl_2, and water convert it into benzaldehyde.

It yields o- and p-nitrotoluene upon nitration, and when it is sulphonated much p-toluene sulphonic and little of the o-acid result.

The action of chlorine upon toluene deserves mention. At boiling temperatures it is exclusively the hydrogen of the side-group which is substituted, and the products are:

Benzyl chloride, $C_6H_5CH_2Cl$,
Benzal chloride, $C_6H_5CHCl_2$,
Benzo-trichloride, $C_6H_5CCl_3$.

o- and p-Chlortoluene, $C_6H_4Cl.CH_3$, are produced in the cold. In the presence of iodine and $SbCl_5$ the chlorine only enters the nucleus even in the cold (Beilstein and Geitner, A. **139**, 311). Phosphorus pentachloride, however, renders the entrance of chlorine into the side-chain more easy (A. **272**, 150).

Hydrocarbons, C_8H_{10}.—Ethyl benzene is isomeric with the three dimethyl benzenes. Iso- or m-xylene, of the three xylenes occurring in coal-tar, is present in the largest amount, and is of technical value.

When the mixture is boiled with dilute nitric acid, the ortho- and para- varieties are changed to their corresponding toluic acids, which are finally oxidized to o- and p phthalic acids. Metaxylene is attacked with more difficulty. Potassium permanganate oxidizes the three xylenes to their corresponding toluic acids and these to phthalic acids. On shaking crude xylene with ordinary sulphuric acid, the ortho- and meta- xylenes dissolve to form sulphonic acids, which are separated through their salts and sulphamides (B. **10**, 1013; **14**, 2625). p-Xylene volatilizes first when crude xylene is distilled with steam.

o-**Xylene** is obtained from brom-toluene by means of CH_3I and sodium. Potassium permanganate oxidizes it to phthalic acid. Chromic acid decomposes it, like many other o-diderivatives, into carbon dioxide and water.

m-**Xylene**, or **Isoxylene.**—The production of mesitylene by the distillation of mesitylenic acid with lime is of great theoretical importance. This reaction genetically links m-xylene to mesitylene, in which the [1,3,5]-position of the three methyl groups may be demonstrated. This, then, would also prove the m-position for the toluic acid and phthalic acid resulting from the oxidation of m-xylene (p. 37).

$$\underset{\text{Mesitylene}}{C_6H_3\left\{\begin{matrix}[1]\ CH_3\\ [3]\ CH_3\\ [5]\ CH_3\end{matrix}\right.} \longrightarrow \underset{\text{Mesitylenic Acid}}{C_6H_3\left\{\begin{matrix}[1]\ CO_2H\\ [3]\ CH_3\\ [5]\ CH_3\end{matrix}\right.} \longrightarrow \underset{\text{Isoxylene}}{C_6H_4\left\{\begin{matrix}[1]\ CH_3\\ [3]\ CH_3\end{matrix}\right.} \longrightarrow \underset{\text{m-Toluic Acid}}{C_6H_4\left\{\begin{matrix}[1]\ CO_2H\\ [3]\ CH_3\end{matrix}\right.} \longrightarrow \underset{\text{Isophthalic Acid.}}{C_6H_4\left\{\begin{matrix}[1]\ CO_2H\\ [3]\ CO_2H\end{matrix}\right.}$$

p-**Xylene** is formed when camphor is distilled with $ZnCl_2$. It is obtained pure by the action of sodium and CH_3I upon p-bromtoluene and p-dibrombenzene (B. **10**, 1355). Dilute nitric acid oxidizes it first to p-toluic acid and subsequently to terephthalic acid. Chromic acid converts it immediately into the latter acid. Paraxylene is soluble in fuming sulphuric acid only; its sulphonic acid forms large crystals, and is not very soluble.

Ethyl Benzene, $C_6H_5.C_2H_5$, also present in coal tar, is produced by the action of sodium upon C_6H_5Br and C_2H_5Br, and hydriodic acid upon styrolene, $C_6H_5.C_2H_3$, but best by the action of C_2H_5Br and $AlCl_3$ upon benzene (B. **22**, 2662). Dilute nitric acid and chromic acid oxidize it to benzoic acid; CrO_2Cl_2 converts it into phenyl acetaldehyde, $C_6H_5.CH_2.CHO$.

Hydrocarbons, C_9H_{12}.—The isomerism of the eight compounds of this formula has been mentioned (p. 52): three trimethyl benzenes, three

methyl ethyl benzenes, and two propyl benzenes. The physical constants of these eight hydrocarbons are given in the table exhibited on p. 53.

Mesitylene, *symmetrical trimethyl benzene*, $C_6H_3(CH_3)_3$, occurs in coal tar, and is produced by distilling acetone (Kane, 1837) or allylene with concentrated sulphuric acid (p. 42; compare B. **29**, 958, 2884).

The proof of its symmetrical structure (p. 37) is of fundamental importance in determining the position of benzene substitution products. Dilute nitric acid converts mesitylene into mesitylenic acid, mesidic acid or uvitic acid, and trimesic acid:

$$C_6H_3\begin{cases}[1]CH_3\\ [3]CH_3\\ [5]CH_3\end{cases} \rightarrow C_6H_3\begin{cases}[1]CO_2H\\ [3]CH_3\\ [5]CH_3\end{cases} \rightarrow C_6H_3\begin{cases}[1]CO_2H\\ [3]CO_2H\\ [5]CH_3\end{cases} \rightarrow C_6H_3\begin{cases}[1]CO_2H\\ [3]CO_2H\\ [5]CO_2H\end{cases}$$

Mesitylene — Mesitylenic Acid — Uvitic Acid — Trimesic Acid.

Pseudocumene, [1,3,4]-*trimethyl benzene*, also occurs in coal tar. It is separated from mesitylene by means of its more difficultly soluble sulpho-acid (B. **9**, 258), from which it is subsequently isolated (p. 51). It is formed from brom-p-xylene and 4-brom-m-xylene. This is evident from its constitution.

Hemimellithene, [1,2,3]-*trimethyl benzene*, occurs in coal tar (B. **19**, 2517), and is obtained from isodurylic acid, $C_6H_2(CH_3)_3.CO_2H$. It may be synthesized by the action of metallic sodium and methyl iodide upon 2-brom-m-xylene.

The three **Ethyl Toluenes** have been prepared from the three brom-toluenes by means of ethyl bromide and sodium. The [1,4]-compound from p-brom-toluene, ethyl bromide, and sodium (B. **28**, 2648), melts at 162°.

n-Propyl Benzene is obtained from C_6H_5Br, n-propyl iodide or bromide and sodium, or from benzyl chloride, by the action of zinc ethide. It can also be produced from benzene by the action of n-propyl bromide and Al_2Cl_6 at −2° (B. **24**, 768).

Isopropyl Benzene, $C_6H_5.C_3H_7$, called **Cumene**, was first made by distilling cumic acid with lime. It can be synthesized by the action of $AlCl_3$ upon a mixture of benzene with isopropyl bromide or chloride, and from benzal chloride, $C_6H_5.CHCl_2$, by means of zinc methide. As n-propyl bromide is rearranged when warm by Al_2Cl_6 into isopropyl bromide, isopropyl benzene is produced in this synthesis with Al_2Cl_6 if the experiment is not conducted in the cold. In the animal organism isopropyl benzene yields propyl phenol (B. **17**, 2551).

Twenty-two isomerides are possible for the *hydrocarbons*, $C_{10}H_{14}$:

$C_6H_2(CH_3)_4$	$C_6H_3\begin{cases}C_2H_5\\ (CH_3)_2\end{cases}$	$C_6H_4\begin{cases}C_2H_5\\ C_2H_5\end{cases}$	$C_6H_4\begin{cases}C_3H_7\\ CH_3\end{cases}$	$C_6H_5.C_4H_9$
3 Isomerides	6 Isomerides	3 Isomerides	6 Isomerides	4 Isomerides.

(*a*) **Tetramethyl Benzenes,** $C_6H_2(CH_3)_4$. The three bodies possible theoretically are known. Symmetrical **Durene** [1,2,4,5], present in coal tar (A. **18**, 3034), is formed from 6-brom-pseudocumene and 4,6-dibrom-m-xylene, by means of CH_3I and sodium; and from toluene by CH_3Cl and $AlCl_3$, as well as from penta- and hexamethyl benzene, by means of Al_2Cl_6. Nitric acid oxidizes it to durylic and cumidic acids, $C_6H_2(CH_3)_2.(CO_2H)_2$ (the symmetrical constitution of durene is concluded from this) (B. **11**, 31). Durene is converted by concentrated sulphuric acid into hexamethyl benzene, and the sulphonic acids of prehnitol, pseudocumene, and isoxylene, which can be separated by means of their amides. Penta-methyl and penta-ethyl benzene undergo similar transpositions.

Isodurene, [1,2,3,5]- or unsymmetrical tetramethyl benzene, is obtained from brom-mesitylene with CH_3I and Na (its constitution follows from this (B. **27**, 3441)); also from camphor by the action of $ZnCl_2$ or iodine (B. **16**, 2259). The oxidation of

isodurene with nitric acid yields 3-isodurylic acid, $C_6H_2(CH_3)_3 . CO_2H$ (B. **15**, 1853), and at last mellophanic acid.

Prehnitol, [1,2,3,4]- or **v-Tetramethyl Benzene**, is produced by the action of methyl iodide and metallic sodium upon 2-brom-pseudocumene and 2,4-dibrom-metaxylene (B. **21**, 2821). Its oxidation by nitric acid produces prehnitylic acid, $C_6H_2(CH_3)_3 . CO_2H$ (B. **19**, 1214) and prehnitic acid, $C_6H_2(CO_2H)_4$.

(*b*) 4-*Dimethyl Ethyl Benzenes*: [1,2,4], boiling at 189°, and [1,3,4] at 184°, and [1,4,3] at 185°, are obtained by the action of $ZnCl_2$ or iodine upon camphor (B. **23**, 988, 2349). The [1,3,5]-body, boiling at 185°, is produced when H_2SO_4 acts upon acetone and methylethyl ketone (B. **18**, 666; **25**, 1533).

(*c*) The three diethyl benzenes yield, first, ethyl benzoic acids and then phthalic acids when they are oxidized.

(*d*) *Methyl-n-propyl Benzenes*: The ortho-body boils at 181°, the meta- at 177°, and the para- at 183°. They result from the action of C_3H_7I and Na upon o-, m-, and p-bromtoluene (B. **24**, 443, 1649; **29**, R. 417).

(*e*) **Methyl-isopropyl Benzenes**: Only the m- and p- bodies are known. The latter is the important cymene. m-Methyl-isopropyl benzene occurs in the light resin oil (A. **210**, 10).

Cymene = [1,4]-*Methyl-isopropyl Benzene* (see table, p. 53) occurs in Roman caraway oil (from *Cuminum cyminum*), together with cumic aldehyde, and in the oil from the seeds of *Cicuta virosa*, in the oil of *Ptychotis ajowan*, in thyme oil, and in the oil from *Eucalyptus globulus*. It is produced on heating thymol, carvacrol, $C_6H_3(OH) . (CH_3) . C_3H_7$, and camphor, with P_2S_5, or with P_2O_5 (A. **172**, 307); also from turpentine oil and other terpenes, $C_{10}H_{16}$, by the withdrawal of two hydrogen atoms. This is effected by heating with SO_4H_2, or with iodine. The production of cymene on boiling cumic alcohol, $C_6H_4(C_3H_7) . CH_2 . OH$ (having the isopropyl group), with zinc dust is especially interesting, as is its formation from geranial (p. 42). Cymene may be synthetically prepared from p-brom isopropyl benzene by means of methyl iodide and sodium. This last reaction explains its constitution (Widman, B. **24**, 439, 970, 1362).

Cymene is a pleasantly smelling liquid. The barium cymene sulphonate, $(C_{10}H_{13}SO_3)_2Ba + 3H_2O$, crystallizing in shining leaflets is characteristic.

Dilute nitric acid or the chromic acid mixture oxidizes cymene to paratoluic acid, $C_6H_4(CH_3) . CO_2H$, and terephthalic acid; whereas in the animal organism or upon shaking with caustic soda and air, it is converted into cumic acid, $C_6H_4(C_3H_7) . CO_2H$.

When concentrated nitric acid acts upon cymene, the product is not nitrocymene, but p-tolylmethyl ketone (B. **19**, 558; **20**, R. 373).

(*f*) **Butyl Benzenes**: *n-Butyl benzene* boils at 180°; *isobutyl benzene* at 167°; *secondary butyl benzene*, at 171°.

Tertiary Butyl Benzene boils at 167°. Bromine does not attack it in the cold or when exposed to sunlight (B. **23**, 2412; **27**, 1610).

Higher toluene homologues:

Hydrocarbons, $C_{11}H_{16}$: **Pentamethyl Benzene** (see table, p. 53) is produced together with hexamethyl benzene when $AlCl_3$ and methyl chloride act upon benzene, toluene, xylene, mesitylene, etc. (B. **20**, 896). For its deportment toward concentrated sulphuric acid see durene (p. 55).

[1,3,5]-**Diethylmethyl Benzene**, boiling at 200°, results from the action of sulphuric acid upon acetone and methylethyl ketone. [1,2,4,5]-**Trimethylethyl Benzene**, *Ethyl Pseudocumene*, boils at 207° (B. **25**, 1530). **Ethyl Mesitylene** boils at 208° (B. **29**, 2459). [1,3]-**Methyl-tert.-butyl Benzene**, boiling at 185–187°, occurs in the essence of resin, the distillation product obtained from pine resin, and is

obtained from the interaction of toluene, isobutyl bromide, and Al_2Cl_6. Its trinitro-derivative is the artificial musk (B. 27, 1606).

Hydrocarbons, $C_{12}H_{18}$.—**Hexamethyl Benzene** (see table, p. 53) is formed by the polymerization of crotonylene on shaking with sulphuric acid, and by heating xylidene hydrochloride and methyl alcohol to 300°. For additional methods of formation see durene and pentamethyl benzene. It does not dissolve in sulphuric acid, as it is incapable of forming a sulpho-acid. Potassium permanganate oxidizes it to benzene hexacarboxylic acid, $C_6(CO_2H)_6$ (*mellitic acid*).

p-Di-n-propyl Benzene, from p-dibrom-benzene, boils at 219°. **p-n-Propyl-iso-propyl Benzene**, from cumyl chloride and zinc ethyl, boils at 212°. Nitric acid oxidizes both to n-propyl benzoic acid, which is isomeric with cumic acid.

Propyl Mesitylene boils at 221° (B. 29, 2459). [1,3,5]-**Triethyl Benzene**, from ethyl methyl ketone by the action of sulphuric acid, boils at 218°. [1,2,3,4]-**Tetraethyl Benzene** boils at 251°. [1,2,4,5]-**Tetraethyl Benzene** melts at +13° and boils at 250°. **Pentaethyl Benzene** (see table, p. 53). **Hexaethyl Benzene** (see table, p. 53) is obtained from C_6H_6, C_2H_5Br, and Al_2Cl_6 (B. 16, 1745; 21, 2819).

The following mono- and dialkylic benzenes with long chains have been prepared by Fittig's reaction from brombenzene and bromtoluene:

n-Octyl Benzene, boiling at 262°; **Cetyl Benzene**, $C_6H_5 . C_{16}H_{33}$, melting at 27° and boiling at 230° (15 mm); **o-Methyl Cetyl Benzene**, melting at 8–9° and boiling at 239° (15 mm.); **m-Methyl Cetyl Benzene**, melting at 10–12° and boiling at 237° (15 mm.); **p-Methyl Cetyl Benzene**, melting at 27° and boiling at 240° (15 mm.); **Octadecyl Benzene**, melting at 36° and boiling at 249° (15 mm.) (B. 21, 3182).

2. HALOGEN DERIVATIVES OF THE BENZENE HYDROCARBONS.

A. BENZENE HALOGEN SUBSTITUTION PRODUCTS.

Benzene being a cyclic triolefine, it can take up six atoms of chlorine or bromine in the sunlight. The products are *benzene hexachloride* and *benzene hexabromide*. These bodies will be discussed later as cyclohexane derivatives, following hexahydro-benzene. The hydrogen atoms in the benzene nucleus, however, are very easily replaced by chlorine and bromine—in fact, more readily than the hydrogen of the paraffins.

Properties and Deportment.—The benzene halogen derivatives are in part colorless liquids, and partly colorless, crystalline bodies. They have a faint, but not disagreeable odor. They are insoluble in water, but dissolve readily in other solvents, and volatilize without decomposition. The para-bodies of the benzene dihaloids are solids at the ordinary temperature. Their melting points lie higher than those of the ortho- and meta-compounds, while their boiling points are lower.

The intimate union of the halogen atoms to the benzene nucleus is striking. They are not displaced, or, at least, with great difficulty, by caustic potash (B. 18, 335; 20, R. 712), by ammonia, cyanide of potassium, etc. (Compare the alkylogens, I, 139.) Metallic sodium withdraws the halogens particularly from brom- and iodbenzenes. This behavior is especially important in the synthesis of the benzene hydro-

carbons (p. 50). The reactivity of chlor-, brom-, and iodbenzene with piperidine, resulting in the formation of *phenyl piperidine* is peculiar (B. **21**, 2279; compare also the nitrohalogen benzene derivatives, p. 67). Sodium amalgam in alcoholic solution or hydriodic acid and phosphorus reduce the halogen substitution products to benzene.

Fluorbenzenes result when hydrofluoric acid is poured upon benzene diazopiperidides (Wallach, A. **235**, 258; **243**, 221):

$$C_6H_5N = N - NC_5H_{10} + 2HFl = C_6H_5Fl + N_2 + NH . C_5H_{10} . HFl.$$

Fluorbenzene, C_6H_5Fl, boiling at 85°, specific gravity 1.0236 (20°/4°), was obtained by heating fluorbenzoic acid with hydrochloric acid.

p-Difluorbenzene, $C_6H_4[1,4]Fl_2$, boils at 88° and has the specific gravity 1.11.

Chlorbenzenes.—*Methods of Formation.*—1. Free chlorine acts sluggishly upon benzene. The action is accelerated by iodine, molybdenum chloride, $MoCl_5$, and ferric chloride, which is particularly well suited for this purpose.

2. The hydroxyl groups of the free phenols are replaced with difficulty by chlorine when phosphorus pentachloride is the reagent. This substitution occurs more readily in the case of the nitrophenols.

3. A very important method that is particularly adapted for the preparation of chlorbenzenes and aromatic halogen derivatives consists in the transformation of the diazo-compounds. The latter are obtained from the amido-bodies, which are the nitro-reduction products. Atomic rearrangement does not occur in these reactions. In the decomposition of the diazo-body the chlorine enters the position which the diazo-, the amido-, and the nitro-group previously held:

$$\underset{\text{Diazobenzene Chloride.}}{C_6H_5N_2Cl} = C_6H_5Cl + N_2$$

Knowing, therefore, when working with the di- and poly-substitution products, the constitution of one of the bodies thus changing, that of the other is necessarily established.

Name.	Formula.	M. P.	B. P.	Density.
Monochlorbenzene,	C_6H_5Cl	−45°	132°	1.128 (0°)
[1,2]-(o)-Dichlorbenzene,	$C_6H_4Cl_2$	—	179°	
[1,3]-(m) Dichlorbenzene,	....	—	172°	
[1,4]-(p)-Dichlorbenzene,	....	+53°	172°	
[1,2,3]-(v)-Trichlorbenzene,	$C_6H_3Cl_3$	16°	218°	
[1,2,4]-unsym. Trichlorbenzene,	....	63°	213°	
[1,3,5]-sym. Trichlorbenzene,	....	54°	208°	
[1,2,3,4]-v-Tetrachlorbenzene,	$C_6H_2Cl_4$	46°	254°	
[1,2,3,5]-unsym. Tetrachlorbenzene,	....	50°	246°	
[1,2,4,5]-sym. Tetrachlorbenzene,	....	137°	244°	
Pentachlorbenzene,	C_6HCl_5	86°	276°	
Hexachlorbenzene,	C_6Cl_6	226°	326°	

The predominating product in the chlorination of chlorbenzene is p-dichlorbenzene. Very little o-dichlorbenzene results (B. **29**, R. 648). p-Dichlorbenzene also results from the action of phosphorus pentachloride upon p-quinone (see this). The behavior of the **dichlorbenzenes**, when nitrated, is characteristic:

o-Dichlorbenzene yields [1,2]-dichlor-4-nitrobenzene, m. p. 43°
m-Dichlorbenzene " [1,3]-dichlor-4- " m. p. 32°
p-Dichlorbenzene " [1,4]-dichlor-3- " m. p. 55°

Hexachlorbenzene, Julin's chloride of carbon, has been prepared by the exhaustive chlorination of many alkyl benzenes and other derivatives of benzene (B. **29**, 875). It is also produced when $CHCl_3$ and C_2Cl_4 are conducted through a tube heated to redness.

Brombenzenes are prepared just like the chlorine substitution products:

(1) By direct substitution by means of bromine carriers, such as aluminium bromide (B. **10**, 971); (2) from phenols; (3) from diazo-derivatives (p. 58):

NAME.	FORMULA.	M. P.	B. P.	DENSITY.
Monobrombenzene,	C_6H_5Br	—31°	155°	1.517 (0°)
[1,2]-o-Dibrombenzene,	$C_6H_4Br_2$	— 1°	224°	2.003 (0°)
[1,3]-m-Dibrombenzene,	. . . .	+ 1°	219°	
[1,4]-p-Dibrombenzene,	. . . .	89°	219°	
[1,2,3]-v-Tribrombenzene,	$C_6H_3Br_3$	87°	—	
[1,2,4]-unsym. Tribrombenzene,	. . . .	44°	275°	
[1,3,5]-sym. Tribrombenzene,	. . . .	119°	278°	
[1,2,3,4] v-Tetrabrombenzene,	$C_6H_2Br_4$	—	—	
[1,2,3,5]-unsym. Tetrabrombenzene,	. . . .	98°	329°	
[1,2,4,5]-sym. Tetrabrombenzene,	. . . .	175°	—	[B. **28**,191]
Pentabrombenzene,	C_6HBr_5	260°	—	
Hexabrombenzene,	C_6Br_6	ab. 315°	—	

In the bromination of hot benzene the chief product is the p-dibrom body, and very little of the o-derivative (B. 10, 1345). The nitration of these dibrombenzenes is characteristic for them:

o-Dibrombenzene yields [1,2]-dibrom-4-nitrobenzene, m. p. 58°.
m-Dibrombenzene yields (1) [1,3]-dibrom-4-nitrobenzene, m. p. 61° [chief product].
(2) [1,3]-dibrom-2-nitrobenzene, m. p. 82° [secondary product].
p-Dibrombenzene yields [1,4]-dibrom-2-nitrobenzene, m. p. 85°.

W. Körner utilizes the production of the tribrombenzenes from the three dibrombenzenes in deducing their constitution (p. 38). *Hexabrombenzene* is also formed upon heating CBr_4 to 300°.

Kekulé heated (200°) benzene with iodine and iodic acid, and thus obtained the **iodbenzenes.** The reaction proceeded in the sense of the equation (A. **137**, 161):

$$5C_6H_6 + 4I + HIO_3 = 5C_6H_5I + 3H_2O.$$

They have been obtained more frequently from the corresponding amido-bodies by aid of the diazo-derivatives (p. 58):

Name.	Formula.	M. P.	B. P.
Iodbenzene,	C_6H_5I	$-30°$	188°
[1,2]-(o)-Di-iodbenzene,	$C_6H_4I_2$	$+27°$	286°
[1,3]-(m)-Di-iodbenzene,	.....	40°	285°
[1,4]-(p)-Di-iodbenzene,	.....	129°	285°

Hexa-iodbenzene, C_6I_6, is formed in the exhaustive iodation of benzene carboxylic acids (benzoic acid, terephthalic acid) with iodine and fuming sulphuric acid. It consists of reddish-brown needles, which melt with decomposition from 140–150° (B. **29**, 1631). See B. **29**, 1405, for bromiodbenzenes.

Iodoso-benzene. Iodobenzene. Diphenyliodonium Hydroxide.—These remarkable bodies were obtained from *phenyliod-chloride* (Willgerodt, 1886), which contains two atoms of chlorine combined with iodine; it may be derived from iodine trichloride, ICl_3 (see Inorganic Chemistry).

Phenyliod-chloride, $C_6H_5ICl_2$, consists of yellow needles. It is produced when chlorine is conducted into a solution of iodbenzene in chloroform. When it is shaken with caustic alkali iodoso-benzene results:

$$C_6H_5ICl_2 + 2KI = C_6H_5IO + 2KI + H_2O.$$

Iodosobenzene, C_6H_5IO, is an amorphous substance. It explodes at about 210°. When it is treated with an acidulated solution of potassium iodide it gives off its oxygen with the separation of an equivalent amount of iodine:

$$C_6H_5IO + 2KI + 2CH_3.COOH = C_6H_5I + 2CH_3COOK + 2I + H_2O.$$

It has a basic character and forms salts, which are derived from the hypothetical hydrate $C_6H_5I(OH)_2$—*e. g.*, $C_6H_5I(OOC.CH_3)_2$; hence $C_6H_5ICl_2$ should be regarded as iodosobenzene hydrochloride.

Iodobenzene, $C_6H_5IO_2$, is formed when iodosobenzene is heated alone or boiled with water:

$$2C_6H_5IO = C_6H_5I + C_6H_5IO_2,$$

or by the oxidation of iodosobenzene with hypochlorous acid, or upon treating phenyl-iod-chloride with a bleaching lime solution (B. **29**, 1567). Iodobenzene explodes at 227–230°. Its deportment is like that of a superoxide.

Diphenyliodonium Hydroxide, $(C_6H_5)_2IOH$, is only known in aqueous solution. It is formed on shaking a mixture of iodoso- and iodobenzene with moist silver oxide:

$$C_6H_5IO + C_6H_5IO_2 + AgOH = (C_6H_5)_2I.OH + IO_3Ag.$$

Its iodide results on boiling iodobenzene with a solution of potassium iodide (B. **29**, 2008). Diphenyliodonium hydroxide has a strong alkaline reaction and forms salts: $(C_6H_5)_2I.I, (C_6H_5)_2ICl, (C_6H_5)_2INO_3$, which recall the salts of thallium (compare ammonium compounds, 1, p. 168; metallo-organic derivatives, 1, p. 182). The *carbonate* and *nitrate* are very soluble; the *chloride* and *bromide* form white precipitates. **Diphenyliodonium Iodide,** $(C_6H_5)_2I.I$, is polymeric with iodbenzene. It consists of yellow needles, which dissolve with difficulty in alcohol, and melt, with production of iodbenzene, at 175–176° (V. Meyer, B. **27**, 1592; **28**, R. 80).

B. HALOGEN DERIVATIVES OF THE ALKYL BENZENES.

Under the conditions observed with benzene itself—in the cold, in the presence of iodine, with molybdenum pentachloride, or ferric chloride—the atoms of chlorine or bromine enter the nucleus of the alkyl benzenes. The *aromatic* substitution products result. Thus, toluene affords:

$$C_6H_5CH_3 \longrightarrow C_6H_4Cl.CH_3 \longrightarrow C_6H_3Cl_2.CH_3, \text{ etc.}$$
$$C_6H_5CH_3 \longrightarrow C_6H_4Br.CH_3 \longrightarrow C_6H_3Br_2.CH_3, \text{ etc.}$$

In the case of boiling benzene homologues the substitution takes place almost exclusively in the hydrogen of the side-chain, and *aliphatic* substitution products result. Thus, toluene yields

$$C_6H_5CH_3 \longrightarrow \underset{\text{Benzyl Chloride}}{C_6H_5CH_2Cl} \longrightarrow \underset{\text{Benzal Chloride}}{C_6H_5CHCl_2} \longrightarrow \underset{\text{Benzotrichloride.}}{C_6H_5CCl_3}$$

These are compounds corresponding to:

$$\underset{\text{Ethyl Chloride}}{CH_3.CH_2Cl} \longrightarrow \underset{\text{Ethidene Chloride}}{CH_3.CHCl_2} \longrightarrow \underset{\text{Methyl Chloroform.}}{CH_3.CCl_3}$$

and will be considered at the conclusion of the oxygen derivatives which correspond to them:

$$\underset{\text{Benzyl Alcohol}}{C_6H_5.CH_2OH} \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} \longrightarrow \underset{\text{Benzoic Acid.}}{C_6H_5CO_2H}$$

into which they can be easily transformed, and from which they can be obtained by the use of phosphorus pentachloride.

In sunlight chlorine and bromine also act substitutingly in the cold upon the aliphatic side-chains (B. 20, R. 530). Chlorine converts boiling isopropyl benzene into p-chloroisopropyl benzene (B. 26, R. 771). Phosphorus trichloride also attacks the alkyls of the alkyl benzenes at the boiling temperature.

The other two methods which may be considered in the production of halogen derivatives of benzene—the action of phosphorus halides upon oxybenzenes and the transformation of corresponding diazo-bodies—yield alkyl benzenes, with substitutions in the nucleus. Naturally, a substitution can occur both in the nucleus and in the aliphatic residue of the same alkyl benzene. The halogen atoms which have entered the side-chain are always reactive, and can readily be exchanged for radicals, whereas the halogen atoms which have entered the benzene nucleus are very intimately combined. The aromatic mono-halogen derivatives of the alkyl benzenes, especially the bromalkyl benzenes, have been largely used in the synthesis of higher alkyl benzenes, following the method discovered by Fittig (p. 50). The oxidation of the side-chains to carboxyl groups is very important for the determination of constitution. It is in this way that any halogen atoms present in the side-chains can be determined (p. 52).

Sodium amalgam in alcoholic solution will replace the halogen atoms with hydrogen. Hydriodic acid will do the same.

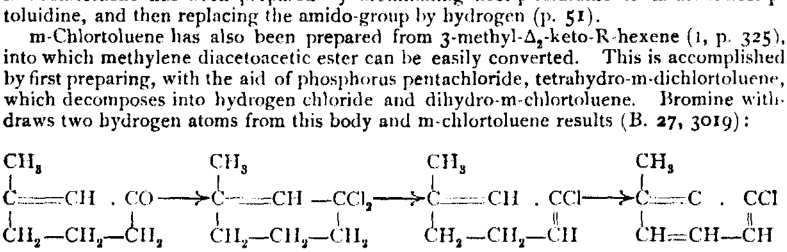
The aromatic halogen substitution products of the alkyl benzenes are exceedingly numerous. Their simplest representatives are the monohalogen toluenes, which are tabulated for more complete review:

NAME.	FORMULA.	M. P.	B. P.
[1,4]-, p-Fluortoluene, ...	$CH_3[1]C_6H_4[4]Fl$	—	117°
[1,2]-, o-Chlortoluene, ...	$CH_3[1]C_6H_4[2]Cl$	—34°	156°
[1,3]-, m-Chlortoluene, ...	$CH_3[1]C_6H_4[3]Cl$	—48°	150°
[1,4]-, p-Chlortoluene, ...	$CH_3[1]C_6H_4[4]Cl$	+ 7°	163°
[1,2]-, o-Bromtoluene, ...	$CH_3[1]C_6H_4[2]Br$	—26°	181°
[1,3]-, m-Bromtoluene, ...	$CH_3[1]C_6H_4[3]Br$	—40°	183°
[1,4]-, p-Bromtoluene, ...	$CH_3[1]C_6H_4[4]Br$	+ 28°	184°
[1,2]-, o-Iodtoluene, ...	$CH_3[1]C_6H_4[2]I$	—	204°
[1,3]-, m-Iodtoluene, ...	$CH_3[1]C_6H_4[3]I$	—	204°
[1,4]-, p-Iodtoluene, ...	$CH_3[1]C_6H_4[4]I$	35°	211°

p-Fluortoluene has been prepared by the method used for fluorbenzene. The chlorination and bromination of toluene in the cold, or in the presence of iodine or Fe_2Cl_6, results in the formation of para- and ortho-derivatives in almost equal quantities. p-Chlortoluene can be separated from its ortho-isomeride by heating with sulphuric acid to 150°, when the o-body passes into its sulpho-derivative.

All the monochlor-, monobrom-, and monoiod-toluenes are obtained pure by decomposing the diazo-compounds made from the three amido-toluenes or toluidines (p. 58). o- and p-Toluidines are easily obtainable from the corresponding nitrotoluenes (p. 68). m-Bromtoluene has been prepared by brominating acet-p-toluidine to m-brom-acet-p-toluidine, and then replacing the amido-group by hydrogen (p. 51).

m-Chlortoluene has also been prepared from 3-methyl-Δ_2-keto-R-hexene (1, p. 325), into which methylene diacetoacetic ester can be easily converted. This is accomplished by first preparing, with the aid of phosphorus pentachloride, tetrahydro-m-dichlortoluene, which decomposes into hydrogen chloride and dihydro-m-chlortoluene. Bromine withdraws two hydrogen atoms from this body and m-chlortoluene results (B. 27, 3019):



If we start with ethidene diacetoacetic ester, the product will be [1,3,5]-chlor-m-xylene (B. 29, 310). [1,3,6]-Chlorcymene has been similarly prepared from menthone or ketohexahydrocymene (B. 29, 314).

The iodoso- and iodo-compounds corresponding to p-iodtoluene are known (B. 26, 358; 27, 1903).

The conversion of the halogen toluenes into solid nitrohalogen toluenes and their oxidation to halogen benzoic acids of known constitution are distinguishing characteristics. When heated with a chromic acid mixture (see aromatic acids) the p- and m-derivatives are oxidized to the corresponding substituted benzoic acids, whereas the o-derivatives are attacked with difficulty and completely destroyed. When boiled with dilute nitric acid, with potassium permanganate, or ferricyanide of potassium, all three isomerides (even the ortho) are oxidized to acids.

Six isomeric aromatic dihaloid toluenes, with similar halogen atoms, are possible. The six dichlortoluenes are known (B. 29, R. 867). They are isomeric with benzal chloride, $C_6H_5CHCl_2$, and with the chlorbenzyl chlorides, $ClC_6H_4CH_2Cl$. All of the six isomeric dibromtoluenes have also been prepared. Pentabromtoluene has been obtained from suberane and bromine (p. 28).

The appended table contains the easily accessible bromine derivatives of the polymethyl benzenes:

NAME.	M. P.	B. P.
[1,2,4]-Brom-o-xylene,	— 2°	214°
[1,3,4]-Brom-m-xylene,	—	203°
[1,4,2]-Brom p-xylene,	+ 9°	200°
Tribromhemimellithene (p. 53),	245°	—
[1,2,4,3]-Monobrompseudocumene (p. 53),	—	237°
[1,2,4,3,6]-Dibrompseudocumene,	64°	293°
Tribrompseudocumene,	224°	—
Monobrom-mesitylene (p. 53),	— 1°	225°
Dibrom-mesitylene,	+ 60°	285°
Tribrom-mesitylene,	224°	—
Monobromprehnitol (p. 53),	30°	265°
Dibromprehnitol,	210°	—
Monobromisodurene (p. 53),	—	253°
Dibromisodurene,	209°	—
Monobromdurene (p. 53),	61°	262°
Dibromdurene,	199°	317°
Brompentamethyl Benzene,	160°	289°

It is also remarkable that concentrated sulphuric acid is even capable of carrying bromine atoms as it does alkyl groups (p. 51). Thus, concentrated sulphuric acid first converts monobromdurene into dibromdurene, and then into durene (B. 25, 1526).

3. NITROGEN DERIVATIVES OF THE BENZENE HYDROCARBONS,

In which the nitrogen-containing residue is joined to the benzene nucleus by means of or through nitrogen.

These compounds can be classified according to the number of nitrogen atoms contained in the residues. The first class embraces only those in which a single nitrogen atom is present. The *nitro-* compounds are placed at the head of this division. They are very important benzene derivatives. They constitute the starting-bodies for the preparation of the succeeding groups. The *amido-* compounds attach themselves to them. In this class belong the generators of numerous coal-tar dyes and aromatic derivatives having therapeutic value. The *nitroso-* and *β-hydroxylamine* bodies constitute the transition between these two groups.

In the second class are those compounds whose nitrogen residues contain two and more nitrogen atoms in union with each other. The *nitroamines*, the *nitroso-β-hydroxylamines*, the *nitrosamines*, the *azoxy-derivatives*, the *hydrazines*, the *diazo-* and the *azo-compounds* contain two nitrogen atoms. The *nitrosohydrazines*, the *diazoamido-bodies*, and the *azo-imido compounds* contain three nitrogen atoms, while four nitrogen atoms

are present in the ***diazohydrazido-*** or ***buzylene*** derivatives, and the ***tetrazones***, and five in the ***disazoamido-compounds***.

The study of some of these classes has also been of the greatest importance for the chemistry of inorganic nitrogen compounds. If we imagine these eighteen groups of aromatic nitrogen bodies derived from inorganic nitrogen-containing substances, whose formulas can be obtained by the substitution of hydrogen for the aromatic residues, it will be discovered that six of these eighteen forms occur free or in the form of inorganic derivatives of known bodies. In the following table they appear in black-face type:

1.	*Nitro*-compounds, ...	derived from		$\mathbf{H.NO_2}$
2.	*Nitroso*-compounds, ...	"	"	$H.NO$
3.	*β-Hydroxylamine* compounds, ...	"	"	$\mathbf{H.NHOH}$
4.	*Amido*-compounds, ...	"	"	$\mathbf{H.NH_2}$
5.	*Nitroamines*, ...	"	"	$\mathbf{H.NH.NO_2}$
6.	*Nitroso-β-hydroxylamines*, ...	"	"	$H.N(OH).NO$
7.	*Nitrosamines*, ...	"	"	$H.NH.NO$
8.	*Azoxy-compounds*, ...	"	"	$H.N\overset{O}{\frown}N.H$
9.	*Hydrazines*, ...	"	"	$\mathbf{H.NH.NH_2}$
10.	*Diazo*-compounds, ...	"	"	$H.N=N.OH$
11.	*Azo*-compounds, ...	"	"	$H.N=N.H$
12.	*Nitrosohydrazines*, ...	"	"	$H.N(NO).NH_2$
13.	*Diazoamido*-compounds, ...	"	"	$H.N=N.NH_2$
14.	*Diazo-oxyamido*-compounds, ...	"	"	$HN=N—NHOH$
15.	*Azoimido*-compounds, ...	"	"	$\mathbf{H.N}<\begin{matrix}\mathbf{N}\\ \Vert\\ \mathbf{N}\end{matrix}$
16.	*Diazohydrazo-* or *Buzylene* compounds,	"	"	$H.N=N.NH.NH_2$
17.	*Tetrazones*, ...	"	"	$H.NH.N=N.NH.H$
18.	*Disdiazoamido* derivatives, ...	"	"	$H.N=N.NH.N=N.H.$

The first three groups will be treated in the preceding order. The nitroso-*β*-hydroxylamines (6) attach themselves to the *β*-hydroxylamines (3). Then follow the amido-derivatives (4), the nitrosamines (7), the nitroamines (5), the diazo-derivatives (10), the diazoamido-bodies (13), the disdiazoamido- (18), the diazo-oxyamido- (14), and the azoimido-compounds (11). The next in order are the azoxy- (8) and the azo-bodies (11). The last to be considered are the hydrazines (9), the nitrosohydrazines (12), the tetrazones (17), and the diazohydrazo- or buzylene derivatives (16). This arrangement is justified by the genetic relations of the individual classes of bodies to one another, and they should have preference over the purely systematic arrangement.

1. NITRO-DERIVATIVES OF BENZENE AND THE ALKYL BENZENES.

Benzene and alkyl benzenes containing hydrogen in the nucleus readily yield nitro-derivatives by the action of nitric acid:

$$C_6H_6 + NO_2OH = C_6H_5NO_2 + H_2O.$$

These compounds are more or less yellow in color; the nitrogen of

the nitro-group is in direct union with a carbon atom, as in nitromethane. By reduction they yield amido-bodies:

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O.$$

In a preceding section mention was made that all of the hydrogen in benzene could be replaced by chlorine or bromine. The case is different on introducing nitro-groups. The first two nitro-groups can be introduced quite easily, the third with difficulty, and thus far not more than three nitro-groups have been introduced into one benzene residue.

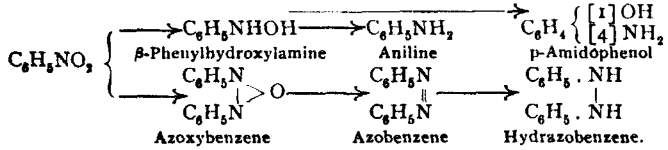
A mixture of nitric acid (1 part) and sulphuric acid (2 parts) acts more energetically than nitric acid alone, as the second acid combines with any water that may be formed in the reaction. Di- and tri-nitro-compounds are the chief products. The nitration is considerably moderated by previously dissolving the substance in glacial acetic acid. The more alkyl groups there are in a benzene hydrocarbon, the more readily will it be nitrated.

The production of nitrophenols in the nitration of benzene hydrocarbons may be explained by assuming an addition of nitric acid at the double union of the benzene ring, with the splitting-off of nitrous acid on the one side and water on the other (B. 24, R. 721). On heating alkyl benzenes with dilute nitric acid, the nitro group enters the aliphatic side-chain. The resulting bodies will be more fully described after the corresponding alcohols (B. 27, R. 193). The aromatic amines, obtained by the reduction of nitro-compounds, can easily be changed to the latter through the diazo-derivatives, when nitrous acid salts yield *nitro-bodies* with cuprous oxide. Nitro-compounds have also been obtained by the direct oxidation of amines—*e. g.*, nitrobenzene, by the action of potassium permanganate upon aniline.

Properties and Deportment.—The nitrohydrocarbons are only slightly soluble in water, but they do dissolve in concentrated nitric acid, and are precipitated from this solution by water. They are very soluble in alcohol, ether, glacial acetic acid, etc. The melting points of the nitro-bodies are usually higher than those of the corresponding bromine derivatives. Their easy reduction is especially interesting.

The β-phenylhydroxylamines have been found to be intermediate products in their conversion into amido-derivatives. Just as two ketone molecules in their reduction combine to a pinacone molecule, so two nitrobenzene molecules, by reduction with alcoholic potash, give off oxygen and form azoxybenzene, which can easily be reduced to azo- and hydrazobenzene.

These relations are made evident in the following diagram:



In the electrolytic reduction of nitro-bodies dissolved in sulphuric acid amidophenols are formed together with the amidohydrocarbons. This is due to a rearrangement of the unstable β-phenylhydroxylamines, or rearrangement and decomposition of intermediate azoxy-derivatives (B.

29, R. 230). In hydrochloric acid solution it is very probable that p-chloranilines are similarly produced (B. 29, 1894).

Because of the ready reduction of the nitro-bodies to compounds, many of which meet with the most varied application in the coal tar color manufacture, there attaches to them the importance of the more valuable and indispensable intermediate products.

When the polynitrohydrocarbons are oxidized with an alkaline ferricyanide solution they are changed to polynitrophenols. The nitro-groups in many polynitrohydrocarbons are exchanged for chlorine when they are heated to 200–300° with hydrochloric acid. Sometimes further chlorination occurs to a certain degree (B. 29, R. 594).

Nitrobenzenes.—The following table contains the melting and boiling points of the six known nitrobenzenes:

NAME.	FORMULA.	M. P.	B. P.
Nitrobenzene,	$C_6H_5NO_2$	+ 3°	205°
[1,2]-, o-Dinitrobenzene,	$C_6H_4(NO_2)_2$	116°	319° (773 mm.)
[1,3]-, m-Dinitrobenzene,	. . . . . .	90°	303° (771 mm.)
[1,4], p-Dinitrobenzene,	. . . .	172°	299° (777 mm.)
[1,2,4]-, unsym. Trinitrobenzene,	$C_6H_3(NO_2)_3$	57°	—
[1,3,5]-, sym. Trinitrobenzene,	. . . .	121°	—

Nitrobenzene, $C_6H_5NO_2$, was discovered in 1834 by Mitscherlich (Pogg. Ann. 31, 625) on treating benzene with nitric acid. It is also produced in the oxidation of aniline (p. 74). It is technically prepared on a large scale, and worked up into aniline and azobenzene. In making it commercially a mixture of nitric and sulphuric acids is allowed to run with constant stirring into benzene. The benzene is contained in cast-iron cylinders (G. Schultz, Chemie des Steinkohlentheers).

Nitrobenzene is a faintly yellow-colored, strongly refracting liquid, possessing an odor resembling that of benzaldehyde or oil of bitter almonds. Its dilute aqueous solution has a sweet taste (B. 27, 1817) and a specific gravity of 1.20 at 20°. It is poisonous in its action, particularly when its vapor is inhaled. Nitrobenzene is used not only in the preparation of colors, but also in perfumery, and to impart to soap the odor of bitter-almond oil (essence of mirbane). It is quite frequently employed in the laboratory as a solvent. Its behavior when reduced has already been referred to (p. 65); its most valuable technical product is *aniline* (p. 74). In many important reactions nitrobenzene serves as an oxidant (see *rosaniline* and *quinoline*).

Dinitrobenzenes, $C_6H_4(NO_2)_2$.—The melting and boiling points are given above. The three dinitrobenzenes are produced if in the nitration with fuming nitric acid the mixture be boiled a short time. On crystallizing from alcohol, the m compound, formed in greatest quantity, separates first, whereas the o- and p-dinitro-derivatives remain in solution (B. 7, 1372). The meta-body is used in the color industry for the preparation of *m-phenylenediamine*.

p-Dinitrobenzene can also be obtained by oxidizing *p-quinone dioxime* (see this); the o-dinitrobenzene from the residues in the preparation of m-dinitrobenzene by solution in twice their weight of boiling nitric acid and pouring this into five to six times its volume of cold nitric acid, when the o-dinitrobenzene will separate in crystals (B. **26**, 266).

By half reduction the dinitrobenzenes yield nitroanilines, which connect genetically the phenylenediamines with the dibrombenzenes and the benzene dicarboxylic acids, or phthalic acids (p. 38).

Ortho-dinitrobenzene crystallizes in plates, yields o-nitrophenol when boiled with caustic soda, and o-nitraniline when heated with alcoholic ammonia. Other aromatic o-dinitro-bodies behave similarly.

Metadinitrobenzene, when heated with potassium ferricyanide and caustic soda, forms α- or [1,OH,2,4]-dinitrophenol and β- or [1,OH,2,6] dinitrophenol. *m*-Dinitrobenzene, heated with alcoholic potash, has one of its nitro-groups replaced by ethoxyl, with the simultaneous entrance of a cyanogen group and the production of [2]-nitro-[6]-ethoxybenzonitrile (B. **17**, R. 19). It unites with alkali bisulphite, with simultaneous reduction and sulphonation, to form m-nitraniline-p-sulphonic acid (B. **29**, 2448).

Paradinitrobenzene forms colorless needles. m- and p-Dinitrobenzenes form additive compounds with naphthalene (B. **16**, 234). When the dinitrobenzenes are heated with chlorine or bromine to 200°, the nitro-groups are wholly or partially replaced by halogens (B. **24**, 3749).

Trinitrobenzenes.—Melting points, see above. [1,3,5]-, sym. **Trinitrobenzene** is obtained from m-dinitrobenzene, and synthetically on acidulating sodium nitromalonic aldehyde (B. **28**, 2597). [1,2,4]-, unsym. **Trinitrobenzene** is produced by heating p-dinitrobenzene with nitric acid and pyrosulphuric acid to 180°. sym. Trinitrobenzene may be oxidized to picric acid, or [1,OH,2,4,6]-trinitrophenol. It forms additive compounds with aniline, naphthalene, etc. m- and p-Dinitrobenzene, trinitrotoluene, etc., yield similar combinations (B. **13**, 2346; **16**, 234). Aqueous alkalies impart orange-yellow colorations to sym. trinitrobenzene. These are probably due to the formation of unstable salts resulting from the replacement of benzene hydrogen by metals (B. **29**, 848; R. 39).

Nitro-haloid Benzenes.

Formation: (1) Upon nitrating chlor-, brom-, and iod-benzene, p- and o-mononitro-products result; the first in larger quantity. (2) On heating the dinitrobenzenes with bromine or chlorine a nitro-group can be replaced by a halogen. (3) Or the dinitrobenzenes are changed to nitranilines and the amido-group replaced by halogens, effected by means of the diazo-compounds. (4) PCl_5 also converts nitrophenols into chlornitro-derivatives. The nitro-haloid benzenes afford the transition from the dinitro-, nitroamido-, to the haloid-amido- and dihalogen benzenes. They are consequently especially important for the recognition of the connection of the various disubstitution products of benzene:

$$C_6H_4<^{NO_2}_{NO_2} \longrightarrow C_6H_4<^{NO_2}_{NH_2} \longrightarrow C_6H_4<^{NO_2}_{Br} \longrightarrow C_6H_4<^{NH_2}_{Br} \longrightarrow C_6H_4<^{Br}_{Br}.$$

The isomeric mononitro-chlor-, brom-, and iod-benzenes have the following melting points:

	[1,2]	[1,3]	[1,4]
$C_6H_4Cl(NO_2)$	32.5°	44.4°	83°
$C_6H_4Br(NO_2)$	41.5°	56°	126° (B. **29**, 788)
$C_6H_4I\ (NO_2)$	49°	33°	171° (B. **29**, 1880).

Meta-chlornitrobenzene occurs in two physical modifications; if rapidly cooled after fusion, it melts at 23.7°, but in a short time reverts to the stable modification, melting at 44.2°.

Of the numerous nitro-haloid benzenes which have been prepared, mention may yet be made of [1,Cl,3,4]-**Dinitro-chlorbenzene**, which has been obtained, in three very

similar modifications, melting at 36.3°, 37°, and 38° (B. 9, 760), and also of **Trinitrochlorbenzene**, $C_6H_2Cl(NO_2)_3$ (1,3,5,4,Cl), **Picryl Chloride**, obtained from picric acid by the action of PCl_5. It melts at 83°. It is converted into picramide, $C_6H_2(NH_2)\cdot(NO_2)_3$, with ammonia, and into picric acid when boiled with soda.

The halogen atom in every monohaloid nitrobenzene is always more easily exchanged the more numerous the nitro-groups are. Picryl chloride, in its deportment, approaches the acid chlorides. **Trichlordinitrobenzene** melts at 130° (B. 29, R. 1155).

Nitrotoluenes.—[1,2],**o-Nitrotoluene**, $CH_3[1]C_6H_4[2]NO_2$, melting at 10.5°, boiling at 218°, and [1,4]-,**p-Nitrotoluene**, $CH_3[1]\cdot C_6H_4[4]NO_2$, melting at 54° and boiling at 230°, are produced in the nitration of toluene. They are separated by fractional distillation, and when reduced, yield the technically important toluidines. If the nitration be carried on at —55°, five and a half times as much p- as o-nitrotoluene (B. 26, R. 362) will be produced. At higher temperatures fuming nitric acid produces chiefly p-nitrotoluene; whereas, nitric-sulphuric acid at lower temperature yields about 66 per cent. of o-nitrotoluene.

Further nitration of o- and p-nitrotoluene produces [2,4]-**dinitrotoluene**, melting at 70°; [2,5]-**dinitrotoluene**, melting at 48° (B. 21, 433; 22, 2679), and [2,4,6]-**trinitrotoluene**, melting at 82°.

The conversion of o-nitrotoluene by bromine at 170° into dibromanthranilic acid is very remarkable:

$$C_6H_4(NO_2)CH_3 + 2Br_2 + 2H_2O = C_6H_2Br_2(NH_2)CO_2H + 2HBr.$$

Metanitrotoluene (1,3) is formed if acetparatoluidine, $C_6H_4\begin{cases}CH_3\\NH\cdot C_2H_3O,\end{cases}$ is nitrated, and the amido-group replaced by hydrogen (B. 22, 831). It melts at 16° and boils at 230°. Further nitration of m-nitrotoluene produces [3,4]-**dinitrotoluene**, melting at 61°, and [3,5]-**dinitrotoluene**, melting at 92° (B. 27, 2209).

Nitro-products of other Alkyl Benzenes.—The ease with which aromatic nitro-derivatives are produced adapts many of them for the detection and recognition of their parent hydrocarbons. Some of them are:

[4]-**Nitro-o-xylene**, $NO_2[4]C_6H_3[1,2](CH_3)_2$, melting at 29° (B. 17, 160; 18, 2670).

[2,4]-**Dinitro-m-xylene**, melting at 82°. [2,6]-**Dinitro-m-xylene**, melting at 93°. [2,4,6]-**Trinitro-m-xylene**, melting at 182° (B. 17, 2424).

[2]-**Nitro-p-xylene**, *boiling at* 239° (B. 18, 2680). [2,6]-**Dinitro-p-xylene**, melting at 123°, and [2,3]-**dinitro-p-xylene**, melting at 93°, form a double compound, melting at 99° (B. 15, 2304). [2,3,6]-**Trinitro-p-xylene** melts at 137° (B. 19, 145). sym.-**Trinitrochlorxylene** melts at 218° (B 28, 2047).

Nitromesitylene, $NO_2[2]C_6H_2[1,3,5](CH_3)_3$, melts at 44°. **Dinitromesitylene** *melts at* 86°. **Trinitromesitylene** *melts at* 232° *(compare B.* 29, *2201).*

[3,5,6]-**Trinitropseudocumene**, $(NO_2)_3[3,5,6]C_6[1,2,4](CH_3)_3$, melts at 185°.

[4,5,6]-**Trinitro-v-trimethyl Benzene**, $(NO_2)_3[4,5,6]C_6[1,2,3](CH_3)_3$, melts at 209° (B. 19, 2517).

Nitroprehnitol, $NO_2[5]C_6H[1,2,3,4](CH_3)_4$, melts at 61° (B. 21, 905). **Dinitroprehnitol** melts at 178°. **Dinitro-isodurene**, $(NO_2)_2[4,6]C_6(1,2,3,5)(CH_3)_4$, melts at 156°. **Dinitrodurene**, $(NO_2)_2[3,6]C_6[1,2,4,5](CH_3)_4$, melts at 205°.

[2,4,6]-**Trinitro-ψ-butyl Toluene**, $(NO_2)_3[2,4,6]C_6H[1]CH_3[3]C(CH_3)_3$, melting at 96–97°, smells intensely like musk, and occurs in commerce as *artificial musk* (B. 24, 2832).

REGULARITIES IN SUBSTITUTION.

Formation of Diderivatives.—In the chlorination and bromination of benzene and toluene, as well as in the nitration of monohaloid benzenes and toluene, the products are almost exclusively p- and o-diderivatives, whereas in the nitration of benzene m-dinitrobenzene is the predominating product. Phenol, aniline, etc., behave like toluene; the first products are p- and o-diderivatives. Benzene-sulphonic acid, C_6H_5-SO_3H; benzoic acid, $C_6H_5CO_2H$; benzaldehyde, C_6H_5CHO; benzonitrile, C_6H_5CN; acetophenone, $C_6H_5.CO.CH_3$, and some additional compounds with negative side-chains yield meta-derivatives chiefly. The substituents present in the mono-derivatives exert, therefore, a definite, directing influence upon the position in which further substitution is to occur. It is not, however, immaterial in what succession or order the substituents are introduced. When chlorbenzene is nitrated, the principal product is m-nitrochlorbenzene, while in the chlorination of nitrobenzene it is chiefly m-nitrochlorbenzene which results.

See B. 23, 130, upon the dependence of the processes of substitution upon the atomic and radical magnitude of the substituents.

Rule of Crum Brown and J. Gibson.—If the hydrogen compound of the atom or radical, which in the mono-derivative has entered the benzene nucleus, cannot be directly (*i. e.*, in *one* operation) oxidized to the corresponding hydroxyl derivative, then in further substitutions o- and p-derivatives result, while in the opposite case m-derivatives predominate (B. 25, R. 672).

Formation of Triderivatives.—By the further substitution (chlorination, nitration) of the ortho- and para-di-derivatives, the replacing groups enter the para- or ortho-position, so that di-derivatives (1,2) and (1,4) yield the same triderivatives (1,2,4) (A. 192, 219). The meta-di-derivatives [1,3] yield [1,3,4]- and [1,2,3]-tri-derivatives. When both substituting groups are of a strongly acid character, as in m-dinitrobenzene, then [1,3,5]-derivatives result.

Formation of Tetra-derivatives.—If an unsymmetrical tri-derivative (1, 2, 4) be further substituted, unsymmetrical tetra-derivatives (1, 2, 4, 6) are generally produced. Thus, from aniline, $C_6H_5.NH_2$, phenol, $C_6H_5.OH$, etc., we obtain compounds like C_6H_2-$Cl_3.NH_2$ and $C_6H_2(NO_2)_3.OH$ (1, 2, 4, 6)—NH_2 or OH in 1, in which the entering groups occupy the meta-position (2, 4, 6 = 1, 3, 5) with reference to each other. By the elimination of the OH and NH_2 groups in them, we obtain symmetrical tri-derivatives, $C_6H_3X_3$ (1, 3, 5).

2. NITROSO-DERIVATIVES OF BENZENE AND THE ALKYL BENZENES.

Mononitroso-derivatives of the benzene hydrocarbons are universally prepared by oxidizing the corresponding β-hydroxylamine derivatives (see below) in the cold with potassium bichromate and sulphuric acid:

$$C_6H_5NHOH + O = C_6H_5NO + H_2O.$$

They consist of colorless crystals, are very volatile, and in a fused or dissolved condition are green in color. They yield nitro-bodies upon oxidation, and amido-derivatives when they are reduced. They condense with aromatic amines with the exit of water, and yield azo-compounds, while with β-phenylhydroxylamines they form azoxy-bodies and with hydroxylamine the so-called isodiazobenzenes (Bamberger, B. 28, 245, 1218; 29, 102):

$$C_6H_5NO + NH_2.C_6H_5 = C_6H_5N:N.C_6H_5 + H_2O$$

$$C_6H_5NO + NO(OH).C_6H_5 = C_6H_5.N\underset{O}{\diagdown\!\diagup}N.C_6H_5 + H_2O$$

$$C_6H_5NO + NH_2OH = C_6H_5N:N.OH + H_2O.$$

Nitrosobenzene, C_6H_5NO, melting at 68°, was first obtained in solution by the action of nitrosyl bromide upon mercury diphenyl (v. Baeyer, 1874; see B. **30**, 506). It is made by oxidizing β-phenylhydroxylamine, and is produced in small amounts, together with other products, in the oxidation of diazobenzene chloride, and by the action of alkalies upon diazobenzene perbromide, as well as in the distillation of azoxybenzene (*B.* **27**, *1182, 1273*). In addition to the preceding reactions mention may be made of the union of nitrosobenzene with phenylhydrazine, forming diazo oxyamido-benzene, $C_6H_5N:N.N(OH).C_6H_5$ (B. **29**, 103). Two molecules of nitric oxide and nitrosobenzene unite to form diazobenzene nitrate (B. **30**, 512).

o-, m-, p-**Nitrosotoluene**, $CH_3.C_6H_4NO$, melt at 72°, 53°, 48°.

p-**Chlor-** and p-**Brom-nitrosobenzene** melt at 87° and 92°.

p-*Dinitroso-derivatives* result upon oxidizing p-quinodioximes with potassium ferricyanide in alkaline solution—*e.g.*:

p-**Dinitrosotoluene**, $CH_3[1]C_6H_3[2,5](NO)_2$, melting at 133°, from toluquinone-dioxime, $CH_3C_6H_3(NOH)_2$, consists of yellow needles, with an odor like that of quinone. Fuming nitric acid converts them into p-dinitrotoluene, and with hydroxylamine hydrochloride they form toluquinone dioxime (B. **21**, 734, 3319).

3. β-ALPHYLHYDROXYLAMINES.*

These very reactive bodies have been obtained as intermediate products in the reduction of nitro- and nitroso-benzenes. They are very sensitive to alkalies, hence they are best prepared by aid of neutral reducing agents—for example, by the action of aluminium amalgam and water upon the ethereal solutions of the nitrobenzenes (B. **29**, 494, 863, 2307). They reduce an ammoniacal silver solution, and also Fehling's solution.

β-**Phenylhydroxylamine**, C_6H_5NHOH, melting at 81° (its *chlorhydrate* precipitated from ether is a white, crystalline mass), is rapidly oxidized in aqueous solution by the air to azoxybenzene, $C_6H_5N\underset{\diagdown O \diagup}{—}N.C_6H_5$, and by potassium bichromate and sulphuric acid to nitrosobenzene. It combines to $C_6H_5N\underset{\diagdown O \diagup}{—}CH.C_6H_5$ (B. **29**, 3037) with benzaldehyde, with diazobenzene to diazo-oxyamido-benzene, and with nitrous acid to nitrosophenylhydroxylamine. Mineral acids rearrange β-phenylhydroxylamine into p-*amidophenol*; compare similar rearrangements of the aromatic nitramines (diazobenzene acid), nitrosoamines, chloramines, into p-nitro-, p-nitroso-, and p-chloranilines (see these).

β-o-**Tolylhydroxylamine** is an oil. β-m-**Tolylhydroxylamine** melts at 68°. β-p-**Tolylhydroxylamine**, melting at 94°, is converted by dilute sulphuric acid into p-*toluhydroquinone* (B. **28**, 245, 1218, R. 156).

4. NITROSO-β-ALPHYLHYDROXYLAMINES.

β-**Phenylnitrosohydroxylamine**, $C_6H_5N(OH).NO$, melting at 59°, isomeric with diazobenzene acid (see this), is produced when a solution of sodium nitrite acts upon an ice-cold solution of β-phenylhydroxylamine hydrochloride (B. **27**, 1548); further, by the action of hydroxylamine and sodium alcoholate upon nitrobenzene (B. **29**, 1884). When methylated with diazomethane (I, 207) it yields a *methyl ether*, $C_6H_5N_2O(OCH_3)$, melting at 38° (B. **29**, 2412). sym.-**Dinitrophenylnitrosohydroxylamine**, $(NO_2)_2C_6H_3N(OH)NO$, melting at 185°, is obtained from sym.-trinitrobenzene and hydroxylamine (*B.* **29**, *2287*).

5. AMIDO-COMPOUNDS, OR ANILINES.

These are produced by the substitution of amido-groups for the hydrogen of benzene and alkyl benzenes:

$C_6H_5NH_2$	$C_6H_4(NH_2)_2$	$C_6H_3(NH_2)_3$
Aniline, Amidobenzene	Diamidobenzene	Triamidobenzene.

* Alphyl is an abbreviation for alkylphenyl, $C_nH_{2n+1}C_6H_4$ (Bamberger).

Or, they may be considered as ammonia derivatives, from which might be concluded the existence of primary, secondary, and tertiary amines of the benzene series (p. 77):

$C_6H_5 . NH_2$	$(C_6H_5)_2NH$	$(C_6H_5)_3N$
Phenylamine	Diphenylamine	Triphenylamine
$C_6H_5NH . CH_3$		$C_6H_5N(CH_3)_2$
Phenylmethylamine		Phenyldimethylamine.

The true analogues of amines of the fatty series—*e. g.*, $C_6H_5 . CH_2 . NH_2$, benzylamine—are obtained when the hydrogen of the side-chains is replaced by the amido-group. They will be considered after their corresponding alcohols.

A. PRIMARY PHENYLAMINES.

Formation of primary phenylamines, whose amido-groups are in union with the benzene nucleus:

I. *Reduction Reactions.*—1. These amido-derivatives are prepared almost exclusively by the reduction of the corresponding nitro-bodies:

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O.$$

Under suitable conditions the β-phenylhydroxylamines appear as intermediate products of the reduction (p. 65).

The most important methods of reduction are:

(*a*) The action of ammonium sulphide in alcoholic solution (Zinin, 1842):

$$C_6H_5 . NO_2 + 3H_2S = C_6H_5 . NH_2 + 2H_2O + 3S.$$

In using this reaction with polynitro-compounds only one nitro-group is reduced, and there result nitroamido-compounds.

In the case of chlornitrobenzenes the nitro-group is only reduced by ammonium sulphide when it is not *adjacent* to the chlorine or another nitro-group; in the reverse instance sulphur or SH will replace the chlorine or a nitro-group (B. 11, 1156, 2056).

(*b*) Action of zinc and hydrochloric acid upon the alcoholic solution of nitro-compounds (A. W. Hofmann); or iron filings and acetic or hydrochloric acid (Béchamp, 1852). The latter method (iron and hydrochloric acid) is applied technically in the manufacture of aniline and o- and p-toluidine. The explanation of the course of this reaction will be found under aniline (p. 74).

(*c*) Action of tin and hydrochloric acid (Roussin) or acetic acid (B. 15, 2105); or a solution of stannous chloride in hydrochloric acid:

$$C_6H_5 . NO_2 + 3Sn \quad + 6HCl = C_6H_5 . NH_2 + 3SnCl_2 + 2H_2O$$
$$C_6H_5 . NO_2 + 3SnCl_2 + 6HCl = C_6H_5 . NH_2 + 3SnCl_4 + 2H_2O.$$

This method serves also for the quantitative determination of the nitro-groups. If the alcoholic solution of a polynitro-compound be mixed with an alcohol-hydrochloric acid solution of a calculated quantity of $SnCl_2$, it will be possible to effect reduction step by step. In the case of o-p-,[2,4]-dinitrotoluene the [4]-NO_2-group will be reduced; whereas, with alcoholic ammonium sulphide it is the [2]-NO_2-group which sustains reduction (B. 19, 2161).

In many instances the following reducing agents have been applied to advantage: (*d*) Sodium arsenite (J. pr. Ch. [2] 50, 563); (*e*) Zinc dust in alcoholic or ammoniacal solution; (*f*) Ferrous sulphate with baryta water (B. 24, 3193), or ammonia (B. 15, 2294), will serve for the reduction of nitro-bodies soluble in water.

2. The reduction of nitroso-compounds—see nitrosobenzene (p. 70) and nitrosodimethylaniline (p. 94).

3. Reduction of hydrazo-compounds and hydrazines (see these).

II. *Exchange Reactions.*—4. The replacement of an halogen atom or of a nitro-group, an hydroxyl or alkoxyl group by the amido-group. These reactions have special value in the preparation of substituted primary phenylamines, as the monohaloid derivatives, the mononitro-hydrocarbons and phenols only yield traces of the amido-derivatives when heated with ammonia. However, these bodies react the more easily, the greater the number of nitro-groups introduced. [1,2]-Chlor- and bromnitrobenzene, [1,2]-dinitrobenzene, [1,2]-nitrophenol and its alkyl esters, [1,4] chlor- and bromnitrobenzene, [1,4]-nitrophenol and its esters yield nitroamido-derivatives when heated with ammonia. The [1,3]- or meta-derivatives do not react (B. 21, 1541; A. 174, 276).

Phenols can be directly transformed into primary (and secondary) amines by heating them to 300–350° with ammonia-zinc chloride ($ZnCl_2 . NH_3$) (B. 16, 2812; 17, 2635; 19, 2916; 20, 1254). The naphthols react even more readily:

$$C_{10}H_7 . OH + NH_3 \xrightarrow{ZnCl_2} C_{10}H_7NH_2 + H_2O$$

Naphthol Naphthylamine.

5. By heating the alkali sulphonates with sodamide, NH_2Na (B. 19, 902).

III. *Decomposition Reactions.*—6. By heating amido-carboxylic acids:

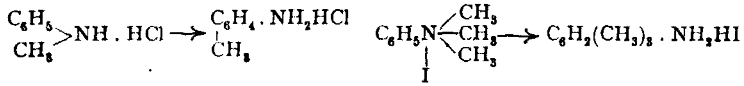
$$(NH_2)_2C_6H_3CO_2H = C_6H_4(NH_2)_2 + CO_2$$

Diamidobenzoic Acids Phenylenediamine.

7. By heating secondary and tertiary amines with hydrochloric acid, and when ammonium bases alone are rapidly heated:

$$C_6H_5NHCH_3 + HCl = C_6H_5 . NH_2 + CH_3Cl$$
$$C_6H_5NHC_2H_5 . HBr = C_6H_5 . NH_2 + C_2H_5Br.$$

IV. *Nucleus-syntheses.*—8. When aniline and methyl chloride are heated some methyl aniline hydrochloride is produced; at higher temperatures this splits into methyl chloride and aniline (see above), and at a still higher temperature (340°) hydrogen in benzene is replaced by methyl and toluidine chlorhydrate is formed. Phenyltrimethyl ammonium iodide yields mesidine hydroiodide:



Phenylmethylamine Chlorhydrate — Toluidine Chlorhydrate — Phenyltrimethyl Ammonium Iodide — Mesidine Hydroiodide.

Secondary and tertiary aromatic bases can be changed to isomeric primary bases in this manner. Instead of the hydrochlorides of the secondary and tertiary bases, salts of primary bases can be heated with suitable alcohols to 300° (B. 13, 1729):

$$C_6H_5NH_2 . HCl + C_4H_9OH = C_4H_9 . C_6H_4NH_2 . HCl + H_2O$$

Aniline Hydrochloride — Isobutyl Alcohol — Amido-tertiary Butyl Benzene.

Or, the free bases can be heated with normal alcohols and zinc chloride to 250° (B. **16**, 105).

Such migrations in the nucleus of atomic groups, which replace an hydrogen of the amido-residue of aromatic amines are more frequently observed; compare phenylhydroxylamine, etc. (p. 70); also B. **29**, R. 870.

Properties and Transformations of the Phenylamines.—The primary amines are colorless, and have a peculiar but not disagreeable odor. They can be distilled under the ordinary pressure without decomposition. They resemble the alkylamines in their ability to form salts (1, 159); they are, however, much less basic than the primary alkylamines. They do not react alkaline, and dissolve with difficulty in water, although they are volatile with steam.

When negative groups enter the primary phenylamines, they further diminish their basic character; the salts of disubstituted anilines, like $C_6H_3Cl_2 . NH_2$ and $C_6H_3(NO_2)_2 . NH_2$, are decomposed by water, or are not produced.

In chemical behavior they approach the acid amides, just as the oxy-compounds or phenols possess the character of acids.

Aniline, as the type of primary phenylamines, will be exhaustively studied.

The following are some of the ordinary reactions of the amido-group:

1. The alkali metals dissolve, when heated, with the evolution of hydrogen. Aniline affords *aniline-potassium*, C_6H_5NHK, and *aniline-dipotassium*, $C_6H_5NK_2$ (p. 75).

2. The halogen alkyls combine with the anilines, forming secondary, tertiary, and finally *quaternary ammonium derivatives* (1, 160).

3. One or two molecules of a primary amine (B. **25**, 2020) will unite with a molecule of an aldehyde. Furfurol and all primary anilines yield intensely red-colored bodies.

4. The deportment of the free primary anilines and their salts toward nitrous acid is exceedingly important for the development of the chemistry of the aromatic bodies. The products are diazoamido-bodies and diazo-compounds. The latter are the intermediate steps in the conversion of the nitro- and amido-derivatives into the most varied substitution products.

5. Thionyl chloride converts primary anilines into *thionyl anilines;* this is similar to the behavior of the primary aliphatic amines (1, 165).

6. An hydrogen atom of the amido-group can be very easily replaced by acid residues; the products are acid anilides, corresponding to the acid amides (1, 164). The acet-derivatives crystallize well and are, therefore, very frequently prepared (p. 82).

7. The primary anilines, like the primary aliphatic amines (1, 166), yield *carbylamines* with chloroform and caustic potash.

8. The primary anilines and carbon disulphide unite to *dialphylsulphoureas* with liberation of hydrogen sulphide, whereas the primary aliphatic amines yield *alkyldithiocarbamic acids* (1, 166).

9. The synthesis of *quinoline* (see this) and other bases containing quinoline nuclei by heating aniline and other primary aromatic bases

with glycerol, sulphuric acid, and nitrobenzene is very suggestive for the development of the chemistry of quinoline. Quinoline derivatives also result in the condensation of fatty aldehydes by means of hydrochloric or sulphuric acid (see quinoline syntheses).

10. *Indols* are produced on heating primary aromatic bases with α-haloid keto-compounds; sometimes *dihydropyrazine derivatives* (see these) are also formed.

Aniline, *Phenylamine*, [Aminophene], [Aminobenzene], $C_6H_5NH_2$, melting at —8°, boiling at 184°, with specific gravity 1.0361 at 0°, is an oil with a faint aromatic odor. It dissolves in 31 parts of water at 12.5° (B. **10**, 709).

History.—Unverdorben first discovered (1826) aniline in the dry distillation of indigo and called it *crystallin*, because of the great crystallizing power of its salts. Runge (1834) found it in coal-tar, and named it *cyanole*, as it gave a blue coloration with a bleaching lime solution. Fritzsche (1841) prepared a base, upon distilling indigo with caustic potash, to which he gave the name aniline, from *Indigofera anil*, the name of the indigo plant. In the same year (1841) Zinin prepared "benzidam" by the reduction of nitrobenzene with ammonium sulphide. A. W. Hofmann (1843) proved the identity of the four bases (A. 47, 37).

Aniline is made upon a commercial basis by reducing nitrobenzene with iron and about $\frac{1}{40}$ of the quantity of hydrochloric acid required by the following equation:

$$C_6H_5NO_2 + 2Fe + 6HCl = C_6H_5NH_2 + Fe_2Cl_6 + 2H_2O.$$

Probably ferrous chloride is the first product, and in its presence the nitrobenzene is reduced by the iron and water, in that the ferrous chloride acts as carrier. The finely divided metal is the immediate active reducing agent (B. 27, 1436, 1815):

$$C_6H_5NO_2 + 3Fe + 6HCl = C_6H_5NH_2 + 3FeCl_2 + 2H_2O$$
$$C_6H_5NO_2 + 2Fe + 4H_2O = C_6H_5NH_2 + Fe_2(OH)_6.$$

The other means of reducing nitrobenzene have already been mentioned on p. 71. In the general methods used in the preparation of primary phenylamines aniline is usually selected as the example. This is the case in the transformation reactions of the primary phenylamines: action of the alkali metals, halogen alkyls, aldehydes, nitrous acid, thionyl chloride, in the acid anilide formation, in the behavior with carbon disulphide, chloroform, and caustic alkali, glycerol, sulphuric acid, and nitrobenzene, etc. Aniline is quite accessible, and it has been drawn into reactions scarcely less frequently than ammonia itself; consequently we shall frequently encounter it as the parent substance, with numerous aromatic compounds. Despite its feeble basic properties, it will precipitate zinc, aluminium, and ferric salts, and on warming will expel ammonia from its salts. This is because of its slight volatility.

Aniline is poisonous. It is a solvent for many bodies—*e. g.*, indigo.

Aniline is very sensitive to oxidizing agents. In the air it gradually assumes a brown color and resinifies. Bleaching lime imparts a purple color to the solution (B. 27, 3263). On adding sulphuric acid and a few drops of potassium chromate to aniline, a red color appears; later it be-

comes an intense blue. If aniline be oxidized with bleaching lime, aided by heat, or with cold potassium permanganate, it will be changed through a series of intermediate products into *nitrobenzene* (B. **26**, 496). Chromic acid converts it into *quinone* (see this), and chlorates in the presence of certain metallic salts change it to *aniline black*.

Aniline is used in the manufacture of numerous technical dyes or compounds with therapeutic value—*e. g.*, aniline black, fuchsine, and others, as well as of *antifebrine*, *antipyrine*, etc., etc.

Aniline Salts.—The *hydrochloride* is obtained perfectly pure and dry by conducting dry hydrogen chloride into an ethereal solution of aniline. It melts at 192°. In commerce it is known as aniline salt. It deliquesces with water. *Platinum Chloride Double Salt* yields yellow needles from alcohol. The *stannous* and *stannic salts*, $SnCl_2 . 2C_6H_5NH_2 . HCl + 2H_2O$ and $SnCl_4 . 2C_6H_5NH_2 . HCl + 2H_2O$. The *sulphate*, $(C_6H_5 . NH_2)_2SO_4H_2$. The *nitrate* crystallizes in large rhombic plates; the *oxalate* forms rhombic prisms. Not only the hydrochloride, but also free aniline combines with certain salts to form double salts. It forms an additive compound with trinitrobenzene (p. 67).

Aniline-potassium, C_6H_5NHK and $C_6H_5NK_2$. They are not known in a pure state. The formation of di- and triphenylamine in the action of brombenzene upon the reaction product resulting from aniline and potassium proves that the hydrogen of the amido-group has been replaced by potassium. Sodium first begins to act upon aniline at 200°; compare further acetanilide (p. 82) and monomethylaniline (p. 78).

Amidomethyl Benzenes.—Some representatives of this group are of the first importance in the color industry. This is particularly true of o- and p-toluidine. Most of the bases are liquids at the ordinary temperatures, but when boiled with glacial acetic acid, with acetyl chloride, or acetic anhydride they readily yield acet-derivatives (p. 82). These substituted acetamides crystallize well, have definite melting points, and are in every way well suited for the recognition of the bases, from which they can be obtained in a very simple way. Therefore, the melting point of the acet-derivative will, in the future, always be given with the boiling point and melting point of the base. The amidomethyl benzenes are made by the reduction of the corresponding nitro-bodies, and by heating under pressure at high temperatures the hydrochlorides of bases which have the methyl groups in union with nitrogen—*e. g.*, dimethylaniline, $C_6H_5N(CH_3)_2$.

Toluidines, $CH_3 . C_6H_4 . NH_2$. The three toluidines are isomeric with benzylamine, $C_6H_5 . CH_2 . NH_2$ (treated after benzyl alcohol), and with methylaniline, $C_6H_5NH . CH_3$ (p. 78). They are made by the reduction of the three nitrotoluenes (p. 68). m-Toluidine is also formed by the reduction of m-nitrobenzal chloride, a transposition product of m-nitrobenzaldehyde (B. **15**, 2009; **18**, 3398). A. W. Hofmann and Muspratt discovered p-toluidine in 1845 (A. **54**, 1).

o-**Toluidine**, liquid, boils at 197°; *Acet-o-toluide* melts at 110° and boils at 296°.

m-**Toluidine**, liquid, boils at 199°; *Acet-m-toluide* melts at 65° and boils at 303°.

p-**Toluidine**, m. p. 45°, boils at 198°; *Acet-p-toluide* melts at 153° and boils at 307°.

gen atom in the para-position with reference to the dialkylamido-group, show a remarkable mobility of this atom of hydrogen, permitting a series of reactions for which the primary and secondary anilines are not adapted, or at least not to so great a degree. The behavior of the phenyldialkylamines toward nitrous acid is particularly important, both theoretically and technically. It converts them into p-nitroso-derivatives.

The three classes of aromatic amines differ therefore from each other in their deportment toward nitrous acid, as follows:

1. Primary phenylamines yield *diazo-derivatives* or *diazoamido-compounds*.

2. Secondary phenylalkylamines yield *nitrosamines*.

3. Tertiary phenyldialkylamines yield p-*nitroso-compounds*.

Other reactions of the phenyldialkylamines will be mentioned after discussing dimethyl aniline.

The methyl- and ethyl-anilines have the following melting points and specific gravities:

Monomethyl Aniline, liquid, boils at 192°; sp. gravity, 0.976 (15°).

Dimethyl Aniline melts at 0.5°, and boils at 192°; sp. gravity, 0.9575 (20°/4°).

Ethyl Aniline, liquid, boils at 206°; sp. gravity, 0.954 (18°).

Diethyl Aniline, liquid, boils at 213.5°; sp. gravity, 0.939 (18°).

The methylated anilines are technically applied in the production of aniline dye-stuffs. They are formed on heating aniline together with HCl-aniline and methyl alcohol to 220°. A better course is to conduct CH_3Cl into boiling aniline.

Methyl Aniline, $C_6H_5 . NH(CH_3)$, is obtained from phenyl carbylamine (p. 83). Its salts (with HCl and H_2SO_4) do not crystallize and dissolve in ether (distinction from the corresponding aniline salts, which are insoluble in this solvent). Bleaching lime imparts no color to it. When methyl aniline is heated to 330°, it is transformed into paratoluidine, $C_6H_4(CH_3) . NH_2$. Methylphenylnitrosamine, see p. 97. Methylacetanilide, see p. 82.

Dimethyl Aniline, $C_6H_5 . N(CH_3)_2$. Its salts do not crystallize. It forms an acetate; this decomposes again into its components on distillation. Hypochlorites do not color it. It forms trimethylphenylium iodide, $C_6H_5 . N(CH_3)_3I$, with methyl iodide.

The action of nitrous acid or, better, sodium nitrite upon the HCl-salt produces p-**Nitroso-dimethyl Aniline.**

p-**Nitro-dimethyl Aniline** is obtained with nitric acid.

Benzoyl chloride and acetyl bromide convert it into benzoyl and acetyl monomethyl aniline, together with trimethylphenylium bromide (B. 19, 1947).

Dimethyl aniline has been introduced into a series of condensation reactions. It combines to p-*amidomandelic acid*, $(CH_3)_2N[4]C_6H_4[1]CH(OH) . CCl_3$, with chloral. Phosgene converts it into *tetramethyl*-p-*diamidobenzophenone*, $[(CH_3)_2N[4]C_6H_4[1]]_2CO$, while with orthoformic ester and zinc chloride it yields *hexamethyl*-p-*leucaniline*, $CH-[C_6H_4N(CH_3)_2]_3$, and with benzotrichloride *malachite green* (see this), etc.

The homologous mono- and dialkyl anilines behave similarly. Mention may also be made of **methylethyl aniline,** $C_6H_5N(CH_3)(C_2H_5)$, boiling at 201°. Its compound with CH_3I is identical with dimethyl-aniline-ethyl iodide; methyl-ethyl aniline-ethyl

iodide is also identical with diethyl aniline-methyl iodide; finally, methyl-propyl aniline-ethyl iodide is identical with ethyl-propyl aniline-methyl iodide—an additional proof that *the five affinities of nitrogen have equal value* (I, 169 and B. **19**, 2785). The higher alkyl is set free from all these ammonium iodides when they are heated with caustic potash.

Alkylen-dianilines: Methylene-diphenyl-diamine, $CH_2(NHC_6H_5)_2$, melting at 65°, is formed from aniline and formaldehyde in alkaline solution, as well as upon heating anhydroformaldehyde-aniline (see below) to 100° with alcoholic aniline (B. **27**, 1806). Hydrochloric acid or aniline hydrochloride rearranges it to diamido-diphenyl methane (compare the *benzidine rearrangement*):

$$CH_2(NHC_6H_5)_2 = CH_2(C_6H_4 . NH_2)_2.$$

Ethylene Diphenyl-diamine, $(C_6H_5 . NH)_2C_2H_4$, from aniline and ethylene bromide, melts at 65°.

Ethylene Monophenyl-diamine, $NH_2 . CH_2 . CH_2 . NH . C_6H_5$, boiling at 263°, has been prepared by means of potassium phthalimide (B. **24**, 2191).

Ethylene Isobutylidene-diphenyl-diamine, $\begin{matrix} CH_2 . N(C_6H_5) \\ | \\ CH_2 . N(C_6H_5) \end{matrix}\!\!>CH . C_3H_7$, melting at 95°, results from ethylenediphenyldiamine and isobutylaldehyde. **Diethylene-diphenyldiamine**, *n-diphenylpiperazine*: see piperazine.

Alkylidene Anilines.—These are produced in energetic reactions by the union of fatty aldehydes and aniline. An exit of water occurs. The simple bodies are usually unstable oils, which immediately polymerize in part like formaldehyde-aniline, or partly condense in an aldol-like manner. The simple and polymeric alkylidene anilines readily absorb hydrocyanic acid and form nitriles of the α-anilido-acids. Those having an aldol nature do not behave in this way; they readily condense, with exit of aniline, to quinoline derivatives (see *quinaldine* syntheses) (B. **25**, 2020).

Anhydroformaldehyde Aniline, $(CH_2NC_6H_5)_3$, melting at 140°, has been prepared by mixing a solution of well-cooled formaldehyde with aniline. It yields methyl aniline upon reduction, and anilido-acetonitrile with prussic acid.

Ethidene Aniline, $CH_3 . CH : N . C_6H_5$, is an oil. It absorbs hydrocyanic acid readily and condenses, without difficulty, to two modifications of **β-anilidobutylidene-aniline**, $CH_3 . CH(NH . C_6H_5)CH_2 . CH : N . C_6H_5$, melting at 126° and at 85°. The latter can be rearranged into the former or high melting body. When heated with hydrochloric or acetic acid they yield quinaldine, while nitrous acid changes them to two dinitroso-compounds, melting at 161° and 120° (B. **29**, 2977). **Aldol-aniline**, $CH_3 . CH(OH)CH_2 . CH : N . C_6H_5$, from aldol and aniline, is a reddish-colored and easily decomposable oil. Ammonium sulphide changes it to **thioaldol aniline**, $CH_3 . CH(OH) . CH_2 . CH\underset{S}{\overset{\quad}{<\!\!-\!\!>}}N . C_6H_5$, melting at 92° (B. **29**, 59).

C. Polyphenylamines.

—The methods of producing these bodies and their behavior will be explained in connection with diphenylamine and triphenylamine.

Diphenylamine, $NH(C_6H_5)_2$, melts at 54° and boils at 310°.

1. This compound is very important from a technical standpoint. It was prepared by A. W. Hofmann (1864) on heating ***aniline blue, rosaniline***, and similar dye-substances (A. **132**, 160).

2. It is made by heating aniline hydrochloride and aniline to 240°:

$$C_6H_5 . NH_2 . HCl + C_6H_5 . NH_2 = (C_6H_5)_2NH + NH_4Cl.$$

The homologous *ditolylamines* have been similarly obtained.

3. It results also upon heating aniline with phenol and $ZnCl_2$ to 260°.

4. It is, furthermore, formed when brombenzene and aniline are heated to 350–390° together with soda-lime (B. **27**, R. 74).

Diphenylamine is a pleasant-smelling, crystalline compound. It is almost insoluble in water, but readily soluble in alcohol and ether. It is a very weak base, whose salts are decomposed by water.

Potassium permanganate, in alkaline solution, oxidizes diphenylamine to *diphenyl-p-azophenylene* or *quinone-dianil*, $C_6H_4\left\{\begin{matrix}[1]N.C_6H_5\\ [4]N.C_6H_5.\end{matrix}\right.$ Chlorine and bromine convert it into tetra- or hexa-halogen substitution products, and nitric acid changes it to the hexanitro-derivative (p. 93). Sulphuric acid dissolves diphenylamine; the solution has a dark-blue color when traces of nitric acid are present: test for nitric acid.

Nitrodiphenylamines (see p. 93).—*Nitrosodiphenylamine* (p. 94). On heating diphenylamine with sulphur it yields *thiodiphenylamine*, $NH<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>S$ (see this), the parent substance of the *thionine* dyes. *Acridines*—*e. g.*, $N\begin{matrix}\diagup C_6H_4 \diagdown\\ \diagdown C_6H_4 \diagup\end{matrix}CH$—are produced when it is heated to 300° with fatty acids. Diphenylamine is applied in the manufacture of *triphenylrosaniline* (see this) or *aniline blue*. *Methyl Diphenylamine*, $CH_3N(C_6H_5)_2$, boils at 292° (A. **235**, 21).

Triphenylamine, $(C_6H_5)_3N$, is obtained on heating dipotassium aniline (p. 75) or sodium diphenylamine with brombenzene (B. **18**, 2156). It crystallizes from ether in large plates, melts at 127° and distils undecomposed. It dissolves in sulphuric acid, forming a violet, then a dark-green color. It cannot form salts with acids. By nitration it yields a trinitro-product, which forms *triamidotriphenylamine*, $N(C_6H_4.NH_2)_3$, by reduction (B. **19**, 759). Hexaphenylrosaniline is produced when phosgene acts upon triphenylamine.

ANILINE DERIVATIVES OF INORGANIC ACIDS.

Aromatic Thionylamines (Michaelis).—These bodies, corresponding to the alkylthionylamines (1, 165), are produced when thionyl chloride acts upon primary bases. This reaction is characteristic of these derivatives. The thionylamines are mostly yellow-colored liquids, boiling at the ordinary pressure without decomposition. They have a peculiar aromatic odor; at the same time the odor of sulphur chloride.

Thionyl Aniline, $C_6H_5N:SO$, boils at 200° and has the specific gravity 1.236 (15°). **Thionyl-o-chloraniline** boils at 207° under 46 mm. pressure; the m-body boils at 233°, and the p-compound melts at 36° and boils at 237°. **Thionyl-o-bromaniline** boils at 210° under 46 mm. pressure; the m-body melts at 32° and the para- at 60°. **Thionyl-o-nitraniline** melts at 32°.

Thionyl-o-toluidine boils at 184° under 100 mm. pressure; the m-compound boils at 220°, while the p-derivative melts at 7° and boils at 224° (A. **274**, 201), etc.

Phenylsulphamic Acid, $C_6H_5NHSO_3H$, only known in the form of salts, is produced when SO_3 or $ClSO_3H$ acts upon aniline dissolved in chloroform (B. **24**, 360), as well as by heating aniline with amidosulphonic acid (B. **27**, 1244). **p-Tolylsulphamic Acid** is precipitated from its ammonium salt solution by acids (B. **28**, 3161). **Sulphanilide,** $SO_2(NHC_6H_5)_2$ (B. **24**, 362).

The aromatic **nitrosamines** and **nitroamines** will be discussed later, before the diazo-derivatives.

Phosphorphenylamines.—Phosphazobenzene Chloride, $C_6H_5N:PCl$, melting at 136–137°, was made by allowing PCl_3 to act upon aniline hydrochloride. Phenol changes it to *Phenoxylphosphazobenzene*, $C_6H_5N:P(O.C_6H_5)$, while with aniline it forms *phosphazobenzene anilide*, $C_6H_5N:P.NH.C_6H_5$ (B. **27**, 490). *Anilido-phosphoric Dichloride*, $C_6H_5NH.POCl_2$, melting at 84°, can be prepared from $POCl_3$ and aniline hydrochloride (B. **26**, 2939). *Orthophosphor-anilide*, $(C_6H_5NH)_3PO$, melts at 208° (A. **229**, 334). *Oxyphosphazobenzene anilide*, $C_6H_5NH.PO:N.C_6H_5$, melting at 357°, is

the final product in the action of $POCl_3$ upon aniline (B. **29**, 716). *Trichlorphosphanil*, $C_6H_5N.PCl_3$ (B. **28**, 2212), is formed from aniline hydrochoride and phosphorus pentachloride.

Sulphophosphazobenzene chloride, $C_6H_5N:PSCl$, melting at 149° and boiling at 280–290°, is formed from $PSCl_3$ and aniline hydrochloride (B. **28**, 1239).

Arsenphenylamines are produced in the action of arsenious chloride or bromide upon aniline dissolved in ether or chloroform. **Arsenanilido-dichloride**, $C_6H_5NHAsCl_2$, melts at 87°. **Arsenanilido-dibromide** melts at 112°. **Arsendianilido-monochloride**, $(C_6H_5NH)_2AsCl$, melts at 127°. **Arsenanilido-dimethyl Ether**, $C_6H_5NHAs(OCH_3)_2$, boils at 55° under 12 mm. pressure (A. **261**, 279).

Silicotetraphenylamide, $Si(NHC_6H_5)_4$, melts at 137° (B. **22**, R. 746).

CARBONIC ACID DERIVATIVES OF THE AROMATIC PRIMARY AND SECONDARY AMINES.

In the introduction to the fatty acids an example was given in connection with acetic acid to show what nitrogen-containing derivatives could be obtained by changes in the carboxyl group (1, 222). The first category contained the acid amides, which may be variously constructed, corresponding to the formulas—

$$1.\ R'.C\begin{cases}=O\\-NH_2\end{cases} \quad \text{and} \quad 2.\ R'.C\begin{cases}-OH\\=NH\end{cases}.$$

The imidoethers are derived from the second formula.

Numerous fatty acid derivatives of these classes have been obtained from aniline and its primary homologues. With acid amides of secondary bases only, formula 1 comes into consideration. In a primary amine both hydrogen atoms are replaceable by acid radicals.

The *thiamides* and *isothiamides* correspond to the acid amides:

$$1.\ R'C\begin{cases}=S\\-NH_2\end{cases} \quad \text{and} \quad 2.\ R'C\begin{cases}-SH\\=NH\end{cases}.$$

The *amide chlorides, imide chlorides,* and the *amidines* attach themselves to these classes.

Anilides of Monobasic Fatty Acids.—The anilides or phenylamides of the fatty acids are made by the methods given for the acid amides (1, 262):

(1) By heating the aniline salts of the fatty acids. (2) By the action of aniline upon esters, (3) upon acid chlorides, and (4) upon acid anhydrides.

The acid anilides are very stable derivatives; can usually be distilled without change, and also directly chlorinated, brominated, and nitrated (p. 77). They furnish a rapid and simple means of distinguishing the aromatic bases. They are resolved into their components by digesting them with alkalies or heating with hydrochloric acid. They yield benzothiazoles when they are heated with sulphur.

The secondary anilides, like secondary alkyl anilines (p. 97), yield *nitrosamines* by the action of nitrous acid.

These give the nitrosamine reaction with phenol and sulphuric acid; but are less stable than the nitrosamines of the secondary anilines. Reducing agents break off

their nitroso-group. The anilides of formic and acetic acids will be described in the following paragraphs:

Formanilide, $C_6H_5.NH.CHO$, is obtained on digesting aniline with formic acid, or by rapidly heating it together with oxalic acid.

It is readily soluble in water, alcohol, and ether. It melts at 46° and boils at 284°, with scarcely any decomposition.

Salts and Alkyl Derivatives.—Concentrated sodium hydroxide precipitates the crystalline compound, $\frac{C_6H_5}{CHO}>NNa$, **Sodium Formanilide**, which methyl iodide changes to **methyl formanilide**, melting at 12.5° and boiling at 253°. The latter is resolved into acid and methyl aniline when it is digested with alcoholic potash or hydrochloric acid (B. **21**, 1107). Silver nitrate added to the alcoholic solution of the sodium compound precipitates *silver formanilide*, $C_6H_5.N:CH(OAg)$. Methyl iodide converts the latter into *methyl isoformanilide*, $C_6H_5.N:CH.O.CH_3$, boiling at 196° (B. **23**, 2274; R. 659). However, the silver salt and acid chlorides—*e. g.*, benzoyl chloride—yield N-derivatives (B. **29**, R. 1141). *Ethyl Isoformanilide, ethoxymethylene aniline*, $C_6H_5N:CHOC_2H_5$, boiling at 212°, is obtained, together with diphenylformamidine, by the prolonged boiling of aniline with orthoformic ester (A. **287**, 360). *Phenylimidoformylchloride-hydrochloride*, $(C_6H_5N=C\genfrac{}{}{0pt}{}{H}{Cl})_2HCl$, is produced when dry hydrochloric acid gas is conducted into an ethereal solution of phenylisocyanide (p. 83) (A. **270**, 303).

Acetanilide, *Antifebrine*, $C_6H_5NH.CO.CH_3$, melting at 112° and boiling at 304°, is produced on boiling aniline with glacial acetic acid (B. **15**, 1977) (for the speed of the reaction consult J. pr. Ch. [2] **26**, 208), or from aniline and acetyl chloride or acetic anhydride, as well as from malonanilic acid (p. 91). Its formation on heating isomeric acetophenone-oxime to 100° with sulphuric acid is especially noteworthy (B. **20**, 2581):

$$C_6H_5C=(NOH).CH_3 \longrightarrow C_6H_5NH.CO.CH_3.$$

Acetanilide crystallized from water, in which it is sparingly soluble in the cold, consists of small white leaflets. It is used as an antipyretic and antirheumatic. Consult A. **184**, 86, for the action of PCl_5. Bisthiazole (see this) is formed when it is heated with sulphur.

Salts.—Its *hydrochloride* is decomposed by water. When it is heated it yields diphenyl ethenylamidine, flavaniline (see this), and dimethyl quinoline (B. **18**, 1340). Ethylaniline, together with acetic acid, is the product on heating acetanilide with sodium alcoholate (B. **19**, R. 680).

Sodium Acetanilide, $C_6H_5NNa.COCH_3$, obtained by the action of sodium upon acetanilide dissolved in xylene, is changed by alkyl iodides into monoalkylacetanilides (B. **10**, 328), from which the monoalkylanilines can be obtained (B. **23**, 2587). The same acetanilides are produced when acetic anhydride acts upon secondary bases. *Mercurio-acetanilide*, $(C_6H_5NCO.CH_3)_2Hg$ (B. **28**, R. 113).

Methyl Acetanilide, *Exalgine*, melts at 101° and boils at 253° (antineuralgic).
Ethyl Acetanilide melts at 54° and boils at 258°.

n-**Propyl Acetanilide** melts at 47° and boils at 266° (B. **21**, 1108).

Substituted Acetanilides.—o- and p-Derivatives of acetanilide are obtained by the action of chlorine, bromine, and nitric acid (p. 92).

Formyl Acetanilide, $C_6H_5N(COH)(COCH_3)$, from mercurio-formanilide and acetyl chloride, melts at 56° (B. **29**, R. 1155).

Diacetanilide, $C_6H_5N(CO.CH_3)_2$, melting at 37° and boiling at 142° under 11 mm. pressure, results when acetanilide is heated to 170–180° with acetyl chloride or with acetic anhydride to 200°, as well as upon boiling phenyl mustard oil with acetic anhydride (B. **27**, 91; **28**, 1665).

The acet-derivatives are characterized by their great power of crystallization. They serve as a means of detecting many primary and secondary aromatic bases. Therefore the melting points of many acet-bodies will be introduced in connection with their respective bases (p. 76).

Nitroso-anilides, see p. 97.

Thioanilides result upon treating the anilides with P_2S_5, and the amidines and isonitriles with H_2S.

Thioformanilide, $C_6H_5 . NH . CHS$, melts at 137° and decomposes at the same time into H_2S and phenyl isocyanide (B. **11**, 338; A. **192**, 85). Consult B. **18**, 2292, upon homologous thioformanilides.

Thioacetanilide melts at 75°. An alkaline solution of potassium ferricyanide oxidizes it to ethenyl amido-thiophenol, $C_6H_4\langle{}^{N}_{S}\rangle C . CH_3$ (B. **19**, 1072).

Methyl-thioacetanilide melts at 58–59° and boils at 290°.

Methyl-isothioacetanilide, $C_6H_5N : C\langle{}^{CH_3}_{SCH_3}$, boiling at 245°, and **Ethyl-isothioacetanilide**, boiling at 250°, are obtained by the action of sodium alcoholate and alkyl iodides upon thioacetanilide (similar to formation of phenyl-isothio urethanes, p. 86, and of phenyl-isothio-ureas, p. 87).

They decompose into aniline hydrochloride and thioacetic ester, $CH_3 . CO . SR$, when shaken with hydrochloric acid (B. **12**, 1061).

Phenylated Amidines of Formic Acid and Acetic Acid.—In addition to the methods proposed for the formation of amidines, the phenylated amidines are produced by the action of PCl_3 or hydrochloric acid upon a mixture of aniline and anilide, when an exit of water occurs (B. **15**, 208, 2449):

$$C_6H_5NHCOCH_3 + C_6H_5NH_2 = \begin{matrix}C_6H_5NH\\C_6H_5N\end{matrix}\rangle C . CH_3 + H_2O.$$

They are feeble bases, and form salts with one equivalent of hydrochloric acid. They break down into aniline and acid anilides when boiled with alcohol.

Diphenyl-formamidine, *Methenyl-diphenyl-diamine*, $C_6H_5N : CH . NH . C_6H_5$, melting at 135°, results upon heating aniline with chloroform or formic acid to 180°, and by boiling phenyl-isocyanide, $C_6H_5 . NC$, with aniline. It crystallizes from alcohol in long needles and distils at 250°, with partial decomposition, into benzonitrile and aniline.

Diphenyl-ethenyl-amidine melts at 131°.

Phenyl-ethenyl-amidine, $C_6H_5N : C(NH_2) . CH_3$, from acetonitrile and HCl-aniline (A. **184**, 362; **192**, 25) (1, 261), is a liquid.

Phenylisuretine, $C_6H_5NH . CH : NOH$, melting with decomposition at 138°, has been obtained from formylchloride-oxime (1, 233) and aniline (B. **27**, R. 745).

Phenylated Carbylamines (1, 236).—**Phenyl isocyanide**, *Phenyl carbylamine*, $C_6H_5N : C$, boils under ordinary pressure at 166° (when polymerization occurs) and unaltered at 64° under a pressure of 20 mm. The colorless liquid soon acquires a clear blue, and finally a dark blue, color, when it resinifies. Its sp. gravity at 15° equals 0.977. Phenyl isocyanide is produced by the action of chloroform on aniline in an alcoholic solution of caustic potash, or by the distillation of thioformanilide (above). It has an exceedingly disagreeable and permanent odor, a bitter taste, and increases the flow of saliva and produces headache.

It behaves as follows: (1) When heated to 220° it is rearranged into *benzonitrile*, C_6H_5CN. (2) Nascent hydrogen converts it into *methyl aniline*. (3) Hydrochloric acid, in dry ether, changes it to *phenylimidoformyl chloride* (p. 82); with (4) glacial acetic acid it yields *formanilide*; with (5) hydrogen sulphide at 100°, *thioformanilide*; (6) with sulphur at 130°, *mustard oil*; (7) with aniline at 170°, *diphenyl formamidine*; (8) with chlorine, *isocyanphenyl chloride* or *phenylimidocarbonyl chloride* (p. 89); (9) with phosgene, *mesoxanilimide chloride*, $C_6H_5N = CCl . CO . CCl = N . C_6H_5$; (10) with acetyl chloride, *pyroracemic anilide chloride* (Nef, A. **270**, 274). **o-Tolylisocyanide** boils at 75° (16 mm.); sp. gravity 0.968 at 24°. **p-Tolylisocyanide** boils at 99° (32 mm.) (B. **27**, R. 792).

Phenylamine Derivatives of Oxy-acids.—These compounds are well adapted for certain condensations in which the benzene hydrogen holding the ortho-position with reference to nitrogen takes part, so that a heterocyclic derivative results. The acids are obtained by heating the corresponding haloid fatty acids with aniline. The nitriles are produced by adding prussic acid to the alkylidene anilines (p. 79), or by heating the aldehyde cyanhydrins with aniline.

Anilido-acetic Acid, Phenyl glycocoll, Phenylglycin, is obtained from chlor- or brom acetic acid by the action of aniline and water (B. **10**, 2046; **21**, R. 136). It melts at 127°.

Its alkyl esters are produced when aniline is heated with the diazo-acetic esters. Its *nitrile*, from anhydroformaldehyde aniline and absolute prussic acid, melts at 43°. If the free acid be heated to 150°, it passes into *diphenylglycin anhydride* or *diphenyldiacipiperazine*, melting at 263° (B. **25**, 2270).

In addition to phenylglycin, aniline and chloracetic acid yield *diglycolphenylamidic acid*, $C_6H_5N(CH_2.CO_2H)_2$, melting at 150–155° (B. **23**, 1990). Its *anhydride*, C_6H_5-$N<{CH_2.CO \atop CH_2.CO}>O$, melts at 148° (B. **25**, 2272). The *imide*, $C_6H_5N<{CH_2.CO \atop CH_2.CO}>NH$, melts at 158° (B. **22**, 1809). The *anil*, $C_6H_5N<{CH_2CO \atop CH_2.CO}>NC_6H_5$, melts at 152° (B. **22**, 1802). When phenylglycin and *bromacetanilide*, $C_6H_5NH.CO.CH_2Br$, melting at 131°, are fused with caustic potash in the air, *indigo* results. The distillation of a mixture of calcium anilido-acetate and formate produces *indol*, $C_6H_4<{CH \atop NH}>CH$ (see this). **Diglycolanilic Acid,** $O<{CH_2.CO.NH.C_6H_5 \atop CH_2.CO_2H}$, melting at 118°, and isomeric with diglycolphenylamidic acid, results from diglycollic anhydride and aniline. Acetyl chloride changes it to *diglycolanil*, $O<{CH_2.CO \atop CH_2.CO}>N.C_6H_5$, melting at 116°, and isomeric with diglycolphenylamidic anhydride (A. **273**, 66).

Thiodiglycol-anilic Acid and Anilide (A. **273**, 70).

o-**Nitrophenylglycin,** $NO_2[2]C_6H_4[1]NH.CH_2.CO_2H$, melts at 193° (see quinoxalines).

a-**Anilidopropionic Acid,** *Phenylalanine*, $C_6H_5NHCH<{CO_2H \atop CH_3}$, melting at 162°, has been prepared from its nitrile, the rearrangement product arising from ethidene cyanhydrin and aniline, as well as from ethidene aniline and prussic acid (B. **15**, 2036; **23**, 2010; **25**, 2032). *β*-**Anilidopropionic Ester,** from *β*-iodpropionic ester, boils at 175° (18 mm.) (B. **29**, 514).

Aniline Derivatives of Ketone Carboxylic Acids.—Pyroracemic Anilide, $CH_3.CO.CO.NH.C_6H_5$, melts at 104°. **Pyroracemic Anilide Chloride,** $CH_3.CO.CCl:N.C_6H_5$, boiling at 136° (13 mm.), is prepared from phenyl carbylamine and acetyl chloride (A. **270**, 299).

Anil-pyroracemic Acid, $C_6H_5.N:C(CH_3).CO_2H$, melting, with decomposition, at 122°, is formed from pyroracemic acid and aniline dissolved in ether (A. **263**, 126). It changes readily into **anil-uvitonic acid,** a derivative of quinoline.

By heating aniline and acetoacetic ester to 130° **Acetoacetanilide,** $CH_2<{CO.CH_3 \atop CO.NH}$.-$C_6H_5$, is produced. It melts at 85°. It condenses to *γ*-methyl carbostyril.

When aniline and acetoacetic ester interact at the ordinary temperature, there is formed anil-acetoacetic ester, that may be considered as *β*-**Phenylimido-butyric Ester,** $CH_3.C(NH.C_6H_5):CH.CO_2.R$, or *β*-**Anilido-crotonic Ester,** C_6H_5N-

$H.C\begin{smallmatrix}CH_3 \\ CH.CO_2R\end{smallmatrix}$. This is a thick oil, boiling without decomposition under 12 mm. pressure. Acids and alkalies decompose it into its components. It condenses to γ-oxyquinaldine (see this) and phenyl lutidon-carboxylic acid (B. **20**, 947 and 1398; **22**, 83).

The tolylamido-derivatives behave similarly (B. **21**, 523).

ANILINE DERIVATIVES OF CARBONIC ACID.

The compounds belonging in this class are very numerous, and will be treated in the order observed with the amine and alkylamine derivatives of carbonic acid, with which they can thus be most satisfactorily compared (see vol. 1).

Carbanilic Acid, phenyl carbamic acid, is not known in a free state. Its esters, called **phenyl urethanes,** result (1) in the action of chlorcarbonic esters upon aniline (B. **18**, 978); (2) from carbanile with alcohols and phenols (B. **3**, 654); (3) from urea chlorides and alcohols (B. **24**, 2108); and (4) from benzoylazide and alcohols (compare 1, 163, and B. **29**, R. 181). The *methyl ester*, $C_6H_5.NH.CO_2CH_3$, melts at 47°, and is converted into amidosulphobenzoic ester when dissolved in sulphuric acid (B. **18**, 980). The *ethyl ester* melts at 52°.

Urea Chlorides are produced by the action of secondary aromatic bases upon phosgene in benzene solution (B. **23**, 424). *Phenyl urea chloride* and *bromide*, $C_6H_5.NH.-COBr$, melt at 67°; compare B. **28**, R. 777.

Methyl Phenyl Urea Chloride, $(CH_3).(C_6H_5)N.COCl$, melts at 88° and boils at 280°. *Diphenyl Urea Chloride*, $(C_6H_5)_2N.COCl$, melts at 85°. When these urea chlorides act upon benzene in the presence of $AlCl_3$ they form the *amides* of benzoic acid (*synthesis of aromatic acids*, B. **20**, 2118; **24**, 2108).

A tetrasubstituted oxamide (B. **25**, 1819, 1825) is produced when sodium in ethereal solution acts upon *di*-p-*tolyl-urea chloride*, melting at 102°.

Phenylated Ureas.—Phenyl urea, $CO\begin{smallmatrix}NH.C_6H_5 \\ NH_2\end{smallmatrix}$, is prepared by evaporating the aqueous solution of aniline hydrochloride and potassium isocyanide (B. **9**, 820), and by the action of ammonia upon carbanile. It melts at 144°.

sym.-*Alkylphenyl Ureas* are produced in the action of aniline upon isocyanic esters, or of phenyl isocyanide (p. 89) upon alkylamines. sym.-*Ethylphenyl Urea*, $C_2H_5NH-CONHC_6H_5$, melts at 99°.

unsym.-*Alkylphenyl Ureas* are obtained from alkyl aniline hydrochloride and potassium isocyanide. unsym.-*Ethylphenyl Urea* melts at 62°.

sym.-**Diphenyl urea,** $CO\begin{smallmatrix}NH.C_6H_5 \\ NH.C_6H_5\end{smallmatrix}$, **carbanilide,** melting at 235° and boiling at 260°, is formed (1) by the action of phosgene gas on aniline (B. **16**, 2301); (2) by the union of carbanile with aniline (A. **74**, 15); (3) by the action of mercuric oxide or alcoholic potash upon s.-diphenyl thiourea (A. **70**, 148), and (4) by heating aniline with urea to 170°. It is most readily obtained (5) by heating monophenyl urea with aniline to 190° (B. **9**, 820), or (6) by heating diphenyl carbonate with aniline to 170° (B. **18**, 516).

Carbanilide consists of silky needles, easily soluble in alcohol and ether, but sparingly soluble in water. Diphenyl urea chloride, heated to 100° with alcoholic ammonia, yields unsymmetrical **diphenyl urea,** $CO\begin{smallmatrix}N(C_6H_5)_2 \\ NH_2\end{smallmatrix}$, melting at 189°, and when distilled yielding diphenylamine and cyanic acid. **Triphenyl urea,** $CO\begin{smallmatrix}N(C_6H_5)_2 \\ NHC_6H_5\end{smallmatrix}$, melting at 136°, and **tetraphenyl urea,** $CO\begin{smallmatrix}N(C_6H_5)_2 \\ N(C_6H_5)_2\end{smallmatrix}$, melting at 183°, have also been obtained from diphenyl urea chloride (B. **9**, 398).

Cyclic Alkylenphenyl Urea Derivatives (compare vol. 1, Derivatives of Urea): *Ethylene Phenyl Urea*, see B. **24**, 2192. *Trimethylene Phenyl Urea* (B., **23**, 1173). *Ethylene Carbanilide*, $CO\begin{smallmatrix}N(C_6H_5).CH_2 \\ | \\ N(C_6H_5).CH_2\end{smallmatrix}$, melts at 183° (B. **20**, 784). *Trimethylene Carbanilide* melts at 153° (B. **20**, 783).

Ureïdes of the Phenylated Ureas of monocarboxylic acids.

Acetyl Phenyl Urea, $CH_3CO . NH . CO . NH . C_6H_5$, melts at 183°. *Acetyl Carbanilide*, $C_6H_5 . NH . CO . N(CO . CH_3)C_6H_5$, melts at 115° (B. **17**, 2882).

Ureïdes of Oxy-acids, Glycolyl-phenylurea, phenyl-hydantoïn, is obtained on heating phenylglycin to 160° with urea. It melts at 160°.

Diphenyl Hydantoïn melts at 139° (B. **25**, 2274).

Phenylated Pseudourea Derivatives.—Ethyl Isodiphenyl Urea, *Anilido-phenyl-carbamic Ethyl Ether*, $C_6H_5N : C(O . C_2H_5)NH . C_6H_5$, is an oil. It results on heating carbodiphenylimide with alcohol to 160–190°, or, better, with sodium alcoholate (B. **27**, 926; **28**, 573).

Phenylated Ureïdes of Carbonic Acid.—Phenylallophanic Ester, $C_6H_5NH . CO . NH . CO_2C_2H_5$, melts at 120° (J. pr. Ch. [2] **32**, 18). **Diphenylallophanic Acid**, see B. **4**, 246. **Diphenylbiuret**, $C_6H_5NH . CO . NH . CO . NH . C_6H_5$, melts at 210° (B. **4**, 265). **Triphenylbiuret** melts at 147° (B. **4**, 250). **Phenylhydroxyl Urea**, $C_6H_5NH . CO . NH . OH$, melts with decomposition at 140°, and results from the action of hydroxylamine hydrochloride upon carbanile (A. **263**, 264).

Phenylsemicarbazide, *Phenylcarbamic Hydrazide*, $C_6H_5NH . CO . NH . NH_2$, melting at 120°, is isomeric with the phenylsemicarbazide or carbamic phenylhydrazide (see this), obtained from phenylhydrazine salts and potassium cyanate. It is also produced by carefully decomposing its *acetyl* derivative with acids. This is formed upon boiling benzazide with acethydrazide in acetone solution; nitrogen is evolved at the same time (B. **29**, R. 982):

$$C_6H_5CON_3 + NH_2 . NH . CO . CH_3 = C_6H_5NH . CO . NHNH . CO . CH_3 + N_2.$$

Phenylated Derivatives of the Thiocarbamic Acids and of Thiourea.—Phenylcarbamic Thiomethyl Ester, $C_6H_5 . NH . CO . SCH_3$, melting at 83°, and the **ethyl ester**, melting at 74°, are formed when diphenylamidine thioalkylens are heated with dilute sulphuric acid to 180° (B. **15**, 339).

Phenyl Sulphurethane, *Xanthogen Anilide, Thiocarbanilic Ethyl Ester*, $C_6H_5NHCS . OC_2H_5$, or $C_6H_5N : C(SH)OC_2H_5$, melting at 71°, is produced when alcohol at 120°, or alcoholic potash, acts upon phenyl mustard oil. It is rearranged by primary and secondary bases into phenyl sulpho-ureas. It breaks down upon distillation into phenyl mustard oil and alcohol (B. **15**, 1307, 2164). Alkaline potassium ferricyanide oxidizes it to *ethoxy-mustard oil*, or ethoxybenzothiazole, $C_6H_4<{N \atop S}>C . O . C_2H_5$ (see this). Like the phenylthioureas (see below), it dissolves in the alkalies, and forms metallic compounds with silver, mercury, and lead.

Phenylimidothiocarbonic Acid, $C_6H_5N : C<{OH \atop SH}$, is not known.

When alkyl iodides act upon the metallic compounds of the phenylsulphurethanes or the free phenylsulphurethanes, we obtain the alkyl derivatives of *phenylimidothiocarbonic acid* (see above). The reaction is very probably analogous to that occurring with the thioacetanilides (p. 83) and the phenyl sulphoureas. The *oxyethylthio-methyl ester*, $C_6H_5 . N : C<{OC_2H_5 \atop SCH_3}$, boils with partial decomposition at 260°. The *di-ethyl* compound melts at 30° (A. **207**, 148).

Phenyl Dithiocarbamic Acid Derivatives.—When the acid is liberated from its salts it decomposes into aniline and CS_2. Its *potassium salt*, $C_6H_5NHCSSK$, is formed when potassium xanthate is boiled with aniline. It consists of golden-yellow needles (B. **24**, 3022). The *methyl ester* melts at 87–88°; the *ethyl* (**Phenyl dithio-urethane**) at 60°. They are produced by warming phenyl mustard oil with mercaptans.

When these dithio-urethanes are heated, they decompose into their generators. They dissolve in alkalies.

Ethyl Phenyldithiourethane, $CS<{N(C_2H_5) . C_6H_5 \atop S . C_2H_5}$, melts at 68° and boils at 310°. It is formed by heating alkylized ethyl diphenyl-amidine thioethyl (p. 87) to 160° with CS_2. These compounds are very stable, no longer soluble in alkalies, and are not desulphurized by mercuric oxide or an alkaline lead solution. They form so-called ad-

dition products (B. 15, 568, 1308) with methyl iodide. Phenyl sulphurethane and diphenyl-thio-urea do the same.

Phenyl thiuramsulphide, $S(CSNHC_6H_5)_2$, melts at 137° (B. 24, 3023).

Methyl phenyl thiocarbamin chloride, $(CH_3)C_6H_5N . CSCl$, melting at 35°, is obtained from methyl aniline and thiophosgene (B. 20, 1631).

Phenyl sulphoureas (compare vol. I: sulphoureas).

Phenylthiurea, $CS\!<\!\begin{smallmatrix}NH . C_6H_5\\ NH_2\end{smallmatrix}$, *Sulphocarbanilamide*, melting at 154°, is formed by the union of phenyl-mustard oil with ammonia.

S is replaced by O and phenylurea formed on boiling with silver nitrate. Mercuric oxide converts it into phenylcyanamide. (For the action of methyl iodide see B. 25, 48.)

s-Diphenyl-thiurea, $CS\!<\!\begin{smallmatrix}NH . C_6H_5\\ NH . C_6H_5\end{smallmatrix}$, *Sulphocarbanilide*, consists of colorless, shining leaflets, melting at 151° (B. 19, 1821), and readily soluble in alcohol. It is produced (1) by the union of phenyl-mustard oil with aniline in an alcoholic solution; (2) by boiling aniline with CS_2 and alcoholic potash with the removal of hydrogen sulphide.

Numerous reactions of sulphocarbanilide are known: (1) Iodine converts it into sulphocarbanile and α-triphenyl-guanidine. (2) When boiled with concentrated hydrochloric acid it decomposes into phenyl-mustard oil and aniline; the mixed symmetrical thiureas, $C_6H_5NH . CS . NH . C_6H_4C_2H_5$, undergo, under like treatment, a decomposition into two mustard oils and two anilines (B. 16, 2016). (3) S is replaced by O, and the product is sym.-diphenylurea, if diphenylthiurea be boiled with mercuric oxide (p. 85). (4) In a benzene solution mercuric oxide produces carbodiphenylimide (p. 90). (5) In the action of ammonia and lead oxide diphenyl-guanidine is produced, while with aniline triphenyl-guanidine is formed.

Phenyl- and sym.-diphenyl-thiureas are soluble in alkalies, forming salts in which the metal is combined with sulphur (as in the case of thioacetanilide, p. 83).

See B. 17, 2088; 23, 815; 26, 1686, upon the alkyl phenyl thiureas.

unsym.-**Diphenylthiurea**, melting at 198°, has been prepared from diphenylamine-sulphocyanide (B. 26, R. 607).

Triphenylthiurea melts at 152° (B. 17, 2092).

Tetraphenylthiurea, $CS\!<\!\begin{smallmatrix}N(C_6H_5)_2\\ N(C_6H_5)_2\end{smallmatrix}$, is obtained by heating triphenylguanidine (p. 88) with carbon disulphide. It melts at 195° (B. 15, 1530).

Phenylthio-hydantoïns.—Although the product formerly regarded as thio- or sulphhydantoïn has proved to be pseudothiohydantoïn (compare vol. I), there are still aromatic phenylsulphydantoïns known.

Phenyl-α-methylsulphydantoïn,

$$\begin{matrix} C_6H_5\text{—}N\text{—}CO \\ CS\diagup \quad | \\ \diagdown NH.CH.CH_3 \end{matrix} \quad \text{or} \quad \begin{matrix} C_6H_5\text{—}N\text{—}CO \\ HS.C\diagup \quad | \\ \diagdown N\text{—}CH.CH_3 \end{matrix},$$

melting at 184°, is produced on melting together phenyl-mustard oil and alanine (B. 24, 3278).

Phenylated Pseudosulphourea Derivatives.—Such compounds are obtained, for example, from phenyl and sym.-diphenyl thiourea by the action of alkyl iodides and caustic alkali, or, better, upon digesting them with alkyl iodides or bromides in alcoholic solution (B. 25, 48). In the second case the iodohydrate of a base is produced. The latter is liberated on treating the former with a sodium carbonate solution, and is capable of taking up additional alkylogen. When digested with alcoholic potash, the imidophenylcarbamic thio-esters split off mercaptans.

Imidophenylcarbamic-thiomethyl Ester, $\begin{smallmatrix}C_6H_5NH\\ NH\end{smallmatrix}\!>\!CS . CH_3$, melts at 71°.

Diphenylamidine-Thiomethyl, Phenylimidophenylcarbamic-thiomethyl Ester, $\begin{smallmatrix}C_6H_5 . NH\\ C_6H_5 . N\end{smallmatrix}\!>\!C . S . CH_3$, melts at 110°, from which would follow that the methyl-group is attached to sulphur. Both these compounds, when heated with dilute sulphuric acid, decompose into thiomethyl phenylcarbaminate.

When heated to 120° with alcoholic ammonia, phenyl-guanidine and mercaptan are obtained.

If heated with carbon disulphide, the products are phenyl-mustard oil, and phenyl-dithiocarbamic esters (B. 15, 343).

With CH_2I_2, $CH_2Br.CH_2Br$, $CH_2Br.CH_2.CH_2Br$, diphenylthiourea affords cyclic derivatives of pseudothiourea (B. 21, 1872):

$$C_6H_5N{=}C{<}\begin{matrix}N{-}C_6H_5\\S{-}CH_2\end{matrix} \qquad C_6H_5N{=}C{<}\begin{matrix}NC_6H_5{-}CH_2\\S{-\!-\!-}CH_2\end{matrix} \qquad C_6H_5N{=}C{<}\begin{matrix}N.C_6H_5{-}CH_2\\S.CH_2{-\!-}CH_2\end{matrix}.$$

The ethylene derivative contains the so-called thiazole ring, while the trimethylene compound contains the pentathiazole ring—the next higher ring, homologous with the thiazole ring.

Pseudo-phenylthiohydantoic acid, $HN:C{<}\begin{matrix}NH.C_6H_5\\S.CH_2.CO_2H\end{matrix}$, melting at 150°, and **Pseudo-diphenylthiohydantoic acid**, $C_6H_5N:C{<}\begin{matrix}NH.C_6H_5\\SCH_2CO_2H\end{matrix}$, are obtained from phenyl- and diphenylthiourea by the action of chloracetic acid. By the elimination of water both of these compounds pass into **psuedo-phenylthiohydantoïn**, $HN:C{<}\begin{matrix}N(C_6H_5)CO\\S{-\!-\!-}CH_2\end{matrix}$, melting at 178°, and **pseudo-diphenylthiohydantoïn**, $C_6H_5N:C{<}\begin{matrix}N(C_6H_5)CO\\S{-\!-\!-}CH_2\end{matrix}$, melting at 176°. Boiling dilute hydrochloric acid converts both compounds, by water absorption, into *phenyl-mustard oil acetic acid*, $OC{<}\begin{matrix}N(C_6H_5)\,CO\\S{-\!-\!-}CH_2\end{matrix}$ (A. 207, 128; B. 14, 1660); ammonia and aniline are liberated simultaneously.

Phenylhydroxy-thio-urea, $C_6H_5.NH.CS.NH.OH$, melting at 106°, is obtained from hydroxylamine and phenyl mustard oil. It decomposes very readily into water, sulphur, and phenylcyanamide (B. 24, 378).

Phenylthiosemicarbazide, $C_6H_5NH.CS.NH.NH_2$, melts with decomposition at 140°. It is formed from phenyl mustard oil and hydrazine hydrate. It is rearranged by aldehydes with the production of hydrazones. Its acidyl derivatives readily part with water and form thiobiazolines (see these). The benzoyl derivative manifests a peculiar behavior in that when it is treated with acetyl chloride it parts with water and a phenyl-imido-phenylthiobiazoline results; with benzoyl chloride, however, a diphenyl triazole mercaptan (see triazoles) is produced (B. 29, 2914):

$$C_6H_5N:C{<}\begin{matrix}NH{-}N\\ \Vert\\ S{-\!-}C.C_6H_5\end{matrix} \longleftarrow C_6H_5NH.CS.NH.NH.CO.C_6H_5 \longrightarrow C_6H_5N{<}\begin{matrix}C(C_6H_5){:}N\\ \vert\\ HS.C{=\!=\!=}N\end{matrix}$$

Phenylated Guanidine Derivatives (see vol. 1, Guanidines).

Diphenyl-guanidine, $HN:C{<}\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}$ (Melaniline), melting at 147°, is produced by the action of cyanogen chloride upon dry aniline, and by digesting cyananilide (p. 90) with aniline hydrochloride. It is, like guanidine, a mono-acid base. Carbon disulphide transforms it into sulpho-carbanilide and sulphocyanic acid.

α-Triphenyl-guanidine, $C_6H_5.N:C{<}\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}$, melting at 143°, is obtained on heating diphenyl-urea or diphenyl-thiurea, alone or with reduced copper, to 140°. It is most readily prepared by digesting an alcoholic solution of diphenyl-thiurea and aniline, with litharge or mercuric oxide (or by boiling with an iodine solution). Heated with CS_2, it reverts again to diphenyl-thiurea and phenyl mustard oil.

β-Triphenyl-guanidine, $C{\begin{matrix}\diagup N(C_6H_5)_2\\ {=}NH\\ \diagdown NH.C_6H_5\end{matrix}}$, melting at 131°, is obtained by heating cyananilide with HCl-diphenylamine. It decomposes into diphenylamine, phenyl mustard oil, and sulphocyanic acid when heated with carbon disulphide.

sym.-Tetraphenyl-guanidine, $NH : C<\substack{N(C_6H_5)_2 \\ N(C_6H_5)_2}$, melting at 130°, is produced by the action of CNCl upon diphenylamine at 170°

Phenylated Nitriles and Imides of Carbonic Acid (compare vol. I).

Phenyl Isocyanate, Carbanile, $CO : N . C_6H_5$, is a mobile liquid, boiling at 163°, and has a pungent odor, provoking tears. It is produced in the distillation of oxanilide, or, better, carbanilic esters with P_2O_5 (B. **25**, 2578 Anm.), also from diazobenzene salts, by the action of potassium cyanate and copper (B. **25**, 1086). It may be most readily obtained by leading $COCl_2$ into fused aniline hydrochloride (B. **17**, 1284), or by heating phenyl mustard oil to 170° with HgO (B. **23**, 1536). Carbanile is perfectly analogous to the isocyanic esters in chemical deportment. It yields diphenylurea with water. It combines with alcohols and phenols to form carbanilic esters; this is a reaction which may be employed in determining *alcoholic hydroxyls* (B. **18**, 2428; 2606). It reacts similarly with the SH-group, as well as with the hydroxyl groups of the aldoximes and ketoximes. It does not react with the groups C : O and C : S (B. **25**, 2578). With ammonia carbanilamide, $CO<\substack{NH . C_6H_5 \\ NH_2}$, is formed.

Diazo-amido-compounds—*e. g.*, $C_6H_5 . N_2 . NHR$—react with phenylisocyanate. In so doing the hydrogen of the amido-group is replaced (B. **22**, 3109).

The preceding reactions, occurring in the absence of water (thus avoiding electrolytic dissociation), proceed in the normal way. Rearrangements do not take place, hence they are well adapted for the *determination of constitution* (Goldschmidt, B. **23**, 2179).

On heating phenylisocyanate with benzene and $AlCl_3$, we get benzoylanilides (see syntheses of benzoic acid and its homologues).

Triphenylisocyanurate, $(CON)_3(C_6H_5)_3$, melting at 275°, is produced (1) by the polymerization of phenylisocyanate upon heating it with potassium acetate (B. **18**, 3225); (2) by heating triphenylisomelamine (p. 90) with concentrated hydrochloric acid to 150° C. Its isomeride is

Triphenylcyanurate, $C_3N_3(O . C_6H_5)_3$. This is produced by the action of cyanogen chloride or cyanuric chloride upon sodium phenate. It melts at 224°.

Isocyanphenyl Chloride, *Phenylimidocarbonyl Chloride*, $C_6H_5N : CCl_2$, boiling at 209° (corr.), is a colorless oil with a penetrating odor. It is produced when chlorine acts upon phenylisocyanide in chloroform solution, and also from phenyl mustard oil and chlorine (B. **26**, 2870). Aniline changes it to α-triphenyl guanidine (A. **270**, 282).

Phenyl-sulphocyanate, $C_6H_5 . S . CN$, boiling at 131°, is isomeric with phenyl mustard oil, and with *Methenyl-amido Thiophenyl*, $C_6H_4<\substack{S \\ N}>CH$ (see amido-thiophenols). It is formed (1) when hydrosulphocyanic acid acts upon diazobenzene sulphate (see this), and (2) cyanogen chloride upon the lead salt of thiophenol. In its reactions it is analogous to the sulphocyanic esters.

Phenyl Mustard Oil, Sulpho-carbanile, *Phenyl-isothiocyanic Ester*, $CS : N . C_6H_5$, is a colorless liquid, with an odor resembling that of mustard oil, and boils at 222°. It is obtained by boiling diphenyl thio-urea with sulphuric or concentrated hydrochloric acid, or, what would be best, with a concentrated phosphoric acid solution (B. **15**, 986), and by the action of an alcoholic iodine solution (with triphenyl guanidine), or $CSCl_2$, upon aniline. It is converted into benzonitrile when heated with reduced copper or zinc-dust.

On this reaction is founded a procedure to replace the group NH_2 by COOH—that is, to convert the anilines successively into thio-ureas, mustard oils, nitriles, and acids. (See synthetic methods of producing the benzoic acids and their homologues.)

If heated with anhydrous alcohols to 120°, or by the action of alcoholic potash, it is converted into phenyl-thio-urethanes (p. 86).

It forms phenyl-thio-ureas with ammonia, the amines, aniline hydrazine, and hydroxylamine. Chlorine converts it into isocyanphenylchloride (see above).

Phenyl mustard oil, under the influence of aluminium chloride, combines with aromatic

hydrocarbons, phenol ethers, and thiophenol ethers, to produce the thioanilides of carboxylic acids (B. 27, 1733).

Phenylated Cyanamide Derivatives (compare cyanamide, vol. 1).

Phenyl Cyanamide, Cyananilide, $C_6N_5 . NH . CN + \frac{1}{2}H_2O$, melts at 47°. When allowed to stand in a desiccator it loses water, becomes liquid, and in moist air reverts to the hydrate. On long standing or when heated it polymerizes to *Triphenyl-isomelamine*. It is formed on conducting CNCl into a cooled ethereal solution of aniline, and by digesting phenyl-thiurea with litharge, or by heating it with lead acetate and alkali (B. 18, 3220). It is readily soluble in alcohol and ether. It forms phenyl-thiurea with H_2S.

Diphenylcyanamide, $(C_6H_5)_2N . CN$, melting at 73°, is formed when an ammoniacal silver solution (B. 26, R. 607) acts upon unsym.-diphenyl thio-urea (p. 87).

Carbodiphenylimide, $C_6H_5N : C : NC_6H_5$, is a thick liquid, which suffers decomposition when distilled at the ordinary pressure, but unaltered at 218° under 30 mm. pressure. Distilled at the ordinary pressure it polymerizes in part to a modification melting at 161°; this has the trebled molecular formula (B. 28, 1004; compare B. 29, 270).

Carbodiphenylimide is produced by the action of mercuric oxide upon sym.-diphenylthiurea in benzene solution, or by the distillation of α-triphenyl-guanidine. When it absorbs water it yields sym.-diphenyl urea. It combines with H_2S to sym.-diphenyl thiurea, and with aniline to α-triphenyl-guanidine. Compare also o-phenylenediamine.

The compounds $C_6H_5N : CCl . NH . C_6H_5$ and $C_6H_5NH . CCl_2 . NH . C_6H_5$ (B. 28, R. 778) are formed when hydrochloric acid gas is conducted into the benzene solution of carbodiphenylimide.

Triphenylmelamine, *Triphenylcyanurtriamide*, $C_3N_3(NH . C_6H_5)_3$, melting at 228°, is produced in the action of cyanuric chloride on aniline, or by heating ethyl trithiocyanuric ester with aniline to 250–300° (B. 18, 3218).

Hexaphenylmelamine, $C_3N_3[N(C_6H_5)_2]_3$, melts at 300°, and is formed by letting cyanuric chloride act upon diphenylamine.

Triphenylisomelamine, $C_3N_3(C_6H_5)_3(NH)_3$, melts at 185°. On long standing phenylcyanamide polymerizes to this compound. Or, it is produced when cyanogen bromide acts on aniline. On warming with hydrochloric acid it successively loses its NH-groups, oxygen entering, and the sole product is the triphenyl ester of isocyanuric acid (p. 89) (B. 18, 3225). In addition to the normal triphenylmelamine and triphenylisomelamine, asymmetrical triphenylamines are known (B. 18, 228).

Anilides of Dicarboxylic Acids.—Oxalic acid and its homologues, as well as the unsaturated dicarboxylic acids, form anilic acids and dianilides, corresponding to the amino-acids and the diamides. Those dicarboxylic acids capable of forming anhydrides yield also anils or phenylimides, corresponding to the imides.

The anilic acids are obtained (1) by partial decomposition of the dianilides; (2) on mixing the ethereal or chloroform solutions of the anhydrides with aniline (B. 20, 3214); (3) by the breaking down of the anils. The latter are reformed from the anilides by treatment with PCl_5 (B. 21, 957), or with acetyl chloride. They also appear on heating the acids or anhydrides with aniline. A large number of these derivatives have been mentioned in the first volume in connection with their respective acids.

Phenylamine Derivatives of Oxalic Acid.—Oxanilic Acid, $C_6H_5 . NH . CO . CO_2H$, melting at 150° (see A. 270, 295, for an isomeric acid melting at 210°), is formed by heating oxalic acid and aniline to 140° (B. 23, 1820), by the action of alcoholic potash upon oxanilide, and when citraconanilic acid is oxidized with potassium perman-

ganate (B. 23, 747). Its *methyl ester* melts at 114° (A. 254, 10), the *ethyl ester* at 66°, and the *chloride* at 82° (B. 23, 1823).

Oxanilide, $(CONHC_6H_5)_2$, melts at 245°. **Tetra-p-tolyloxamide**, $[CON[4]-(C_6H_4[1]CH_3)_2]_2$, from p-ditolylurea chloride, melts at 127° (p. 85). **Oxanildioxime**, $[C:(NOH)(NHC_6H_5)]_2$, formed from *dibromglyoxime peroxide*, melts with decomposition at 215°. *Half-ortho-oxalic-dianilido-methyl Ester*, $CO_2 . CH_3 . C(NH . C_6H_5)_2 . OCH_3$, and *Dimethyl Phenylimido-oxalic Ester*, $CO_2 . CH_3 . C:N . C_6H_5(OCH_3)$, melting at 111°, are obtained from dichlor-oxalic ester and aniline (B. 28, 60).

Phenyloxamic-diphenyl-amidine, $C_6H_5NHCO . C\lessgtr^{NH . C_6H_5}_{N . C_6H_5}$, melting at 134°, is prepared from half-ortho-oxalic ester and oxanildichloride acid ethyl ester (A. 184, 268).

o-**Nitro-oxanilic Acid** melts at 112°. o-**Dinitro-oxanilide** (A. 209, 369).

Malonanilic Acid, $CH_2<^{CO . NH . C_6H_5}_{CO_2H}$, melts at 132° and decomposes into CO_2 and acetanilide. It is produced by a peculiar transposition of acetylphenyl carbaminate of sodium when heated to 140° (B. 18, 1359). PCl_5 converts it into trichlorquinoline (B. 18, 2975).

Malonanilide, $CH_2(CONHC_6H_5)_2$, melts at 223° (B. 17, 135, 235).

Succinanilic Acid and **Succinanil** (see vol. 1, Succinimide).

For **fumaranilic acid, fumaranilic chloride, fumardianilide, maleïnanilic acid, maleïnanil, dichlormaleïnanil, dichlormaleïnanil dichloride, dimethyl dichlormaleïnanilic ester, dichlormaleïnimide anil, dichlormaleïndianil, citraconanilic acid, citraconanil, itaconanilic acid**, consult the corresponding acids described in vol. 1.

Anilido-dicarboxylic Acids.—Compare **phenylasparagine anilic acid, phenylasparagin anil**; for **β-anilidopyrotartaric acid** and **pseudoitaconanilic acid**, see amidosuccinic acids, vol. 1.

Phenylated Ureïdes of Dicarboxylic Acids.—**Phenylparabanic Acid**, $CO<^{N(C_6H_5)-CO}_{NH-\!-\!-CO}$, melting at 208°, and **Diphenylparabanic Acid**, melting at 204°, are formed, for example, by the action of ethoxalic chloride upon the corresponding carbamides (J. pr. Ch. [2] 32, 20).

Aniline Substitution Products.—It is only the aniline derivatives, among the substitution products of the primary phenylmines, which deserve particular consideration, for it was with them that the regularities of substitution obtaining among the aromatic amido-bodies were observed, and they were the intermediate stages in numerous instances where constitution was to be determined.

Aniline Haloids.—*Formation*.—(1) Aniline, like phenol, is more readily substituted than benzene. When chlorine or bromine acts upon the aqueous solutions of aniline salts, the halogen atoms enter the [2,4,6]-position. Starting with acetanilide (p. 82) chlorine and bromine produce first p- and o-monosubstitution products; these are immediately converted into o-p-disubstitution derivatives. If, however, chlorine or bromine be allowed to act upon aniline, in the presence of concentrated sulphuric or hydrochloric acid, m-compounds will be produced. The fact that the amido-group combines with strong acids demonstrates its negative character (B. 22, 2903). The anilines substituted in the meta-position yield tetra- and penta-substitution products (B. 15, 1328).

Iodine can substitute the anilines directly; the resulting hydriodic acid combines with the excess of base: $2C_6H_5NH_2 + I_2 = C_6H_4I . NH_2 + C_6H_5NH_2 . HI$.

2. The monohalogen anilines can be readily obtained from the monohalogen nitro-

benzenes, which in turn are derived from the nitro-amido-derivatives. The change is effected through the diazo-bodies (p. 99)—*e. g.*:

$$C_6H_4<\begin{matrix}NO_2\\NH_2\end{matrix} \longrightarrow C_6H_4<\begin{matrix}NO_2\\Br\end{matrix} \longrightarrow C_6H_4<\begin{matrix}NH_2\\Br\end{matrix}.$$

p-Chloraniline is a stronger base than the o- and m-bodies (B. **10**, 974). It has also been obtained by the electrolytic reduction of nitrobenzene in concentrated hydrochloric acid solution. It is very probable that $C_6H_5 . NHCl$ is formed at first, but subsequently rearranges itself into p-chloraniline (p. 65 and B. **29**, 1895).

	[1,2]-, o-		[1,3]-, m-		[1,4]-, p-		
	M. P.	B. P.	M. P.	B. P.	M. P.	B. P.	
$FlC_6H_4NH_2$, . . .	—	—	—	—	liquid	188°	(A. **243**, 222)
$ClC_6H_4NH_2$, . . .	liquid	207°	liquid	230°	70°	230°	(A. **176**, 27)
$BrC_6H_4NH_2$, . . .	31°	229°	18°	251°	63°	decomposes	(B. **8**, 364)
$IC_6H_4NH_2$, ...	56°	—	27°	—	63°	—	(G. **17**, 487)

Mention may be made of the following higher aniline substitution products. Acetanilide yields:

a-[$1NH_2$,2,4] **Dichloraniline**, melting at 63° and boiling at 245° (B. **7**, 1602).

a-[$1NH_2$,2,4] **Dibromaniline**, melting at 79° (A. **121**, 266).

β-[1,4,$2NH_2$]-**Dichloraniline**, melting at 54° and boiling at 250° (A. **196**, 215) and β-[1,4,$2NH_2$]-**Dibromaniline**, melting at 51° (A. **165**, 180), have been obtained from the corresponding nitro compounds.

Aniline, acted upon by chlorine and bromine, yields:

[$1NH_2$,2,4,6]-**Trichloraniline**, melting at 77° and boiling at 262° (J. pr. Ch. [2] **16**, 449; B. **27**, 3151).

[$1NH_2$,2,4,6]-**Tribromaniline**, melting at 119° (B. **16**, 635).

The five benzene hydrogen atoms in aniline can be substituted by chlorine or bromine:

Pentachloraniline melts at 232°. **Pentabromaniline** melts at 222°. Halogen benzenes are produced by eliminating the amido-group by means of the diazo-compounds (see these).

Nitranilines, $NO_2C_6H_4NH_2$, are isomeric with diazobenzene acid, $C_6H_5NHNO_2$ (p. 99). Nitric acid attacks aniline energetically, and resinifies it with ease.

(1) In order to get mono- and disubstitution products acetanilide is nitrated (p. 82). The amido-group is *protected* by the acetyl group; the immediate products are p- and o-nitracetanilide. When aniline is nitrated in the presence of concentrated sulphuric acid and in the cold, not only p- and o-bodies result, but also metanitraniline (B. **10**, 1716; **17**, 261). The quantity of the latter is greater the more sulphuric acid there is present (p. 91).

The union of the amid-group and the transposition into an acid group occur simultaneously, giving rise to a meta-substitution product (p. 69).

The three isomerides are separated by means of their varying basicity. When their acid solution is neutralized, the m-body is first precipitated, then follow the p- and the o-nitranilines (B. **28**, 1954).

(2) The nitranilines can be prepared by heating haloid nitrobenzenes to 150–180° with alcoholic ammonia; or by heating the ethers of the nitrophenols—*e. g.*, $C_6H_4(NO_2)$.-$O . C_2H_5$, with aqueous ammonia. In both instances the para- and ortho-compounds, and not the meta-, react.

(3) By the partial reduction of polynitro-derivatives (p. 70).

(4) Upon heating nitroamido-benzene sulphonic acids with hydrochloric acid to 170° (B. **18**, 294).

(5) o- and p-Nitranilines are formed in the rearrangement of diazobenzene acid (p. 99):

[1,2]-, o-**Nitraniline** melts at 71°; acet-derivative melts at 92°.
[1,3]-, m-**Nitraniline** " 114°; " " 142°.
[1,4]-, p-**Nitraniline** " 147°; " " 207°.

The nitro-anilines link the diamido- and dinitro-benzenes to the nitro-haloid-, amido-haloid-, and dihaloid benzenes:

$$C_6H_4<^{NH_2}_{NH_2} \leftarrow C_6H_4<^{NO_2}_{NO_2} \rightarrow C_6H_4<^{NO_2}_{NH_2} \rightarrow C_6H_4<^{NO_2}_{Br} \rightarrow C_6H_4<^{NH_2}_{Br} \rightarrow C_6H_4<^{Br}_{Br}$$

When ortho- and para-nitranilines (not meta) are boiled with alkalies, they part with NH_3, and are converted into their corresponding nitrophenols, $C_6H_4(NO_2).OH$; the di- and tri-nitranilines react even more readily.

The nitranilines approach in character the acid amides as the number of nitro-groups in them increases.

Ammonia converts the corresponding dinitrophenols or polynitrohaloid benzenes into:

α-[1NH$_2$,2,4]-**Dinitraniline**, melting at 182°.
β-[1NH$_2$,2,6]-**Dinitraniline**, melting at 138°.

[1NH$_2$,2,4,6]-**Trinitraniline**, $C_6H_2(NO_2)_3.NH_2$, *Picramide*, is obtained from picric acid through its ether, or by means of picryl chloride (p. 68). The latter reacts with ammonia, even in the cold. It forms orange-red needles, and melts at 186°. It forms picric acid when heated with alkalies:

$$C_6H_2(NO_2)_3.NH_2 + KOH = C_6H_2(NO_2)_3.OK + NH_3.$$

sym.-**Trinitroxylidine**, melting at 206°, is obtained from trinitrochlorxylene and ammonia (B. 28, 2047).

Nitrodiphenylamines.—Chlor- and brom-benzene do not react with aniline, but o-bromnitrobenzene and polynitrohaloid benzenes are changed by it into nitrodiphenylamine (together with an aniline halogen hydride). It is also possible to introduce an acid radical—*e. g.*, benzoyl—into the imido-group, and then nitrate. Hexanitrodiphenylamine is produced in the direct nitration of diphenylamine.

o-**Nitrodiphenylamine** melts at 75° (B. 22, 903).
p-**Nitrodiphenylamine** melts at 132° (B. 15, 826).
p-**Dinitrodiphenylamine** melts at 214° (B. 15, 826).

[2,4,6]-**Trinitrophenyl-phenylamine**, from picryl chloride, melts at 175° (B. 3, 126). **Trinitroxyl-phenylamine** melts at 175° (B. 28, 2047).

Hexanitro-diphenylamine is an acid, melting at 238°. It dissolves with a purple-red color, in the alkalies, forming salts. Its ammonium salt occurs in commerce as a brick-red powder. It was employed under the name *Aurantia* before the introduction of the azo-dyes, to color wool and silk a beautiful orange.

NITROSO-DERIVATIVES OF THE PRIMARY, SECONDARY AND TERTIARY AROMATIC AMINES.

Formation.—(1) When the nitrosamines of monomethylaniline or diphenylamine (p. 97) are treated with alcoholic hydrochloric acid, they rearrange themselves into p-nitroso-compounds (B. 19, 2991). (2) The p-nitroso-bodies are also produced when nitrous acid acts upon the tertiary dialkylanilines, or sodium nitrite upon their hydrochlorides (Baeyer and Caro, B. 7, 963). (3) When the nitroso-phenols are fused with ammonium acetate and ammonium chloride, they yield p-nitroso-anilines (B. 21, 729).

Deportment.—When the p-nitroso-derivatives of the secondary and tertiary aromatic amines are heated with caustic soda, they break down into sodium nitrosophenate and alkylamines (1, 163). Most chemists consider the nitroso-phenols to be the monoximes of the paraquinones. And in connection with this mode of formulation of the nitroso-

phenols many are also disposed to view the p-nitroso-derivatives of the secondary and tertiary aromatic amines as quinone derivatives:

$$C_6H_4\begin{cases}[1]:O\\ [4]:O\end{cases} \qquad C_6H_4\begin{cases}[1]:N.OH\\ [4]:O\end{cases} \qquad C_6H_4\begin{cases}[1]:N(CH_3)_2\\ [4]:N\!\!>\!O\end{cases}$$

p-Quinone — p-Quinoxime, p-Nitrosophenol — p-Nitroso-dimethyl-aniline.

p-**Nitroso-aniline**, $NO[4]C_6H_4[1]NH_2$, melting at 174°, crystallizes in steel-blue needles (B. **21**, 729; **28**, R. 735).

p-**Nitrosomethylamine**, $NO[4]C_6H_4[1]NHCH_3$. The free base forms crystals with metallic lustre and melts at 118° C. It is soluble in dilute sodium hydroxide, and is again liberated from its solution by carbon dioxide.

When heated with sodium hydroxide, p-nitrosomethyl aniline is decomposed into sodium nitrosophenate and methylaniline.

p-**Nitroso-mono-ethyl-aniline** melts at 78°.

p-**Nitroso-dimethyl-aniline**, $NO[4]C_6H_4[1]N(CH_3)_2$, melting at 85°, consists of large, green leaflets. Potassium permanganate and ferrocyanide of potassium oxidize it to p-nitrodimethylaniline. Upon reduction it yields p-amidodimethylaniline, which is so important in the dye manufacture. Sodium hydroxide resolves it into nitroso-phenol and dimethyl aniline. Its hydrochloride dissolves with difficulty in cold water. p-**Nitroso-diethyl-aniline** melts at 84°.

p-**Nitroso-diphenylamine**, melting at 143°, consists of green plates, and is produced when hydrochloric acid gas acts upon diphenylnitrosamine (B. **20**, 1252; **21**, R. 227).

C. DIAMINES.

Formation.—The aromatic diamines, whose amido-groups are attached to the benzene nucleus, are formed (1) by the reduction of the three dinitrobenzenes or nitroanilines with tin and hydrochloric acid; (2) the monamines can be converted into the diamines by first changing them to amido-azo-compounds, and then decomposing the latter by reduction:

$$C_6H_5N=N[4]C_6H_4[1]NH_2 + 4H = C_6H_5NH_2 + NH_2[4]C_6H_4[1]NH_2.$$

(3) they can be obtained, also, from the diamidobenzoic acids by the loss of carbon dioxide when they are treated with baryta. This reaction has become of particular importance in ascertaining the constitution of the three phenylenediamines.

(4) Diphenylated diamidobenzenes, $C_6H_4(NH.C_6H_5)_2$, are produced when dioxybenzenes—*e. g.*, *resorcinol* and *hydroquinone* (see these)—are treated with aniline and $CaCl_2$ or $ZnCl_2$.

Properties.—The diamines are colorless solids volatilizing without decomposition, but on exposure to the air they become colored. They are di-acid bases, forming well-defined salts. Ferric chloride imparts an intense red color to their solution. The amide hydrogen atoms can be replaced in the same manner as in the monamines.

Diamidobenzenes, or phenylenediamines, $C_6H_4(NH_2)_2$. The o-body is derived from o-nitraniline by reduction with caustic soda and zinc-dust (B. **28**, 2947). The m-derivative is most easily accessible through m-dinitrobenzene (p. 67). The p-compound is obtained by the decomposition of amido-azo-benzene (Z. f. Ch. (1866) 136).

[1,2]-, o-Phenylenediamine, m. p 102°, b. p. 252°
[1,3]-, m-Phenylenediamine, m. p. 63°, b. p. 287°
[1,4]-, p-Phenylenediamine, m. p. 147°, b. p. 267°.

o-Phenylenediamine is colored red, in hydrochloric acid solution, by ferric chloride, with the production of diamidophenazine hydrochloride (B. **27**, 2782). In the table, see below, showing the numerous o-condensations of which the o-diamines are capable, it is o-phenylenediamine which appears most frequently as the example. o-**Amidophenylurethane** melts at 86°.

m-Phenylenediamine is converted by nitrous acid into *triamido azobenzene* (see this), or *Bismarck brown*. Hence, it imparts an intense yellow color to a dilute solution of nitrous acid, and can therefore be employed for the quantitative estimation of the latter in water (B. **14**, 1015). Consult B. **7**, 1263; **21**, R. 521; **24**, 2113, for the action of $COCl_2$, CS_2, and oxalic ester.

p-**Phenylenediamine** is oxidized by the oxygen of the air to dark garnet-red crystals of **Tetra-amidodiphenyl-p-azophenylene**, $C_6H_4\left\{\begin{array}{l}[1]N[1]C_6H_3[2,5](NH_2)_2\\ \quad | \\ [4]N[1]C_6H_3[2,5](NH_2)_2\end{array}\right.$, melting with decomposition at 230–231° (B. **27**, 480). Manganese dioxide and sulphuric acid convert it into quinone (see this), while bleaching lime changes it to quinonedichloride (see this). p-**Amido-dimethyl aniline**, $NH_2[4]C_6H_4[1]N(CH_3)_2$, melting at 41° and boiling at 257°, is prepared by the reduction of p-nitroso- or p-nitrodimethyl aniline (p. 94), and by decomposing *helianthine* (p. 138), or p-dimethylamido-azobenzene (B. **16**, 2235). Hydrogen sulphide and ferric chloride, in acid solution, impart a dark-blue coloration to its acid solution: *methylene blue* (see this). It is, therefore, a delicate reagent for the detection of hydrogen sulphide. **Formyl-p-amido-dimethyl aniline**, see B. **27**, 602. **Nitro-p-phenylenediamine**, melting at 135°, consists of green, vitreous needles, and is obtained from [1,2,4]-dinitraniline (B. **28**, 1707; **29**, 2284).

Diamidotoluenes, Toluylene Diamines.—The six bodies possible theoretically are known:

1. $[1CH_3, 2,3]$-Toluylene diamine melts at 61° and boils at 255° (A. **228**, 243).
2. $[1CH_3, 3,4]$-Toluylene diamine melts at 88° and boils at 265°.
3. $[1CH_3, 2,4]$-Toluylene diamine melts at 99° and boils at 280° (compare toluylene red).
4. $[1CH_3, 2,6]$-Toluylene diamine melts at 103° and boils at (B. **17**, 1959).
5. $[1CH_3, 3,5]$-Toluylene diamine is a liquid and boils at 284° (A. **217**, 200).
6. $[1CH_3, 2,5]$-Toluylene diamine melts at 64°; boils at 273°.

[1,3,4]-**Toluylene diamine** is the most easily accessible o-diamine. It is prepared from p-acet-toluidine:

$$C_6H_4\left\{\begin{array}{l}[1]CH_3\\ [4]NH\,CO.CH_3\end{array}\right. \longrightarrow C_6H_3\left\{\begin{array}{l}[1]CH_3\\ [3]NO_2\\ [4]NHCOCH_3\end{array}\right. \longrightarrow C_6H_3\left\{\begin{array}{l}[1]CH_3\\ [3]NO_2\\ [4]NH_2\end{array}\right. \longrightarrow C_6H_3\left\{\begin{array}{l}[1]CH_3\\ [3]NH_2\\ [4]NH_2\end{array}\right.$$

[1,2,4]-**Toluylene diamine** is used as the starting-out substance in the preparation of *toluylene red* (see this).

Xylylene Diamines.—[1,3,2,4]-**Diamido-m-xylene** melts at 64° (B. **17**, 2426). [1,3,4,6]-**Diamido-m-xylene** melts at 104°. [1,2,3,5]-,o-**Diamido-m-xylene** melts at 77°.

[1,2,3,5,6]-,o-**Diamidopseudocumene** melts at 90°. [1,4,3,5,6]-,p-**Diamidopseudocumene** melts at 78° (B. **24**, 1647). **Diamidomesitylene** melts at 90° (A. **141**, 134; **179**, 176), etc.

See p. 116 for the di- and tetra-alkylized phenylene diamines. *Phenylated phenylene diamines* or o- and p-*amidodiphenylamine* derivatives are formed in the so-called o- or p-semidine rearrangement of suitable hydrazobenzenes (p. 117).

THE CONDENSATIONS OF THE o-DIAMINES.

The o-diamines possess the power in a remarkable degree of forming condensation products. These usually consist of ring-systems containing five or six atoms, and will be discussed in connection with the *heterocyclic* carbon derivatives. The m- and p-diamines do not possess this power. The condensation occurs in that hydrogen atoms of both amido-groups of an o-diamine are replaced by polyvalent atomic groups. Fre-

quently, when this occurs, the nitrogen atoms occupying the o-position unite with one another.

1. Sulphur dioxide and selenium dioxide convert the o-diamines into *piazthioles* (see these) and *piazselenoles* (see these).

2. Nitrous acid produces *azimides* (see these).

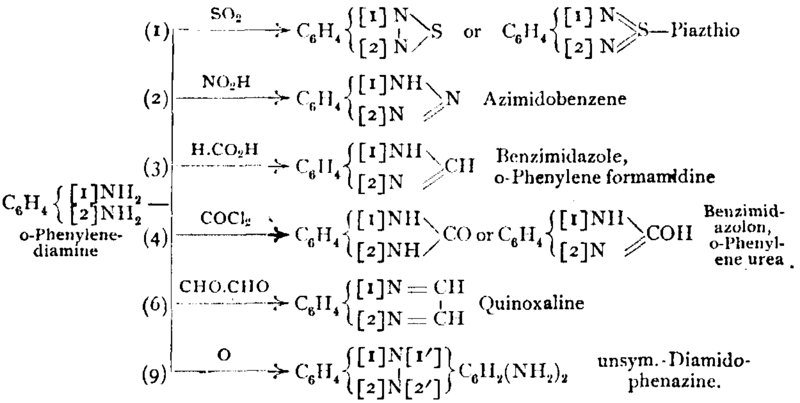
3. The *cyclic amidines* are directly produced from the o-diamines on heating them with acids, their chlorides and anhydrides, as well as with aldehydes: *anhydrobases* or *aldehydines* (Ladenburg). These are substances nearly related to the *glyoxalines* (1, 322) or *imidazoles*, and will be treated later in connection with these. Such condensations have been observed also in the reduction of acidylated o-nitro-amido-compounds (Hobrecker).

4. *Cyclic ureas* and *thiurea derivatives* are formed from $COCl_2$ and $SCCl_2$ or CS_2, also by condensation with urea and thiurea, as well as with ammonium sulphocyanide (p. 97).

5. *Cyclic guanidine* derivatives are obtained by means of carbodiimides (p. 90) and phenyl mustard oils (p. 89).

6. A very interesting condensation of the o diamines is that with glyoxal and other α-dicarbonyl derivatives, as well as with grape-sugar, when *quinoxalines* result, with the exit of water (Hinsberg) (1. 321).

Related six-membered rings are produced (7) when o-diamines condense with cyanogen. (8) By condensation with o-dioxybenzene. (9) unsym.-*Diamidophenazine* is produced by the oxidation of o-phenylenediamine. (10) Dibenzene sulphone-derivatives of o-phenylenediamine condense with alkylen dihaloids—*e. g.*, methylene iodide, ethylene bromide, trimethylene bromide. The products are cyclic diamines, from which the corresponding *phenylene alkylen diamines* are obtained by the splitting off of the benzene sulphone groups (B. 28, R. 756).



The o-*amidophenols* and the o-*amidothiophenols* show condensations similar to those observed with the o-diamines.

DIFFERENCES BETWEEN THE o-, m-, AND p-DIAMINES.

1. The para-diamines are capable of yielding various dyestuffs. Mixed with primary amines (or phenols) and oxidized at the ordinary temperature, they are converted into *indoamine* and *indophenol* dyestuffs; at higher temperatures the so-called *safranines* are produced. When oxidized with ferric chloride in the presence of H_2S, the para-diamines, containing a free NH_2-group, yield sulphurized dyes of thio-diphenylamine (Lauth's Dyestuffs). Manganese dioxide and sulphuric acid oxidize the p-diamines to quinones, recognizable by their odor. Ferric chloride (B. 17, R. 431) imparts color to the diamines. See above, o-phenylendiamine.

2 The ortho-diamines, when acted upon by nitrous acid, yield *azimido*-compounds, *e. g.*, **Azimidobenzene**. The meta-diamines, on the contrary, yield yellow-brown azo-dyes, of the type of phenylene brown. Test for nitrous acid, B. **11**, 624, 627. In very acid solution, and when there is a constant excess of acid (nitrous), the meta-diamines form bisdiazo-derivatives. Nitrous acid (or $NaNO_2$) converts the para-diamines (their salts) into bisdiazo-compounds.

3. When the hydrochlorides of the three isomerides are digested with ammonium sulphocyanide, disulphocyanides, like $C_6H_4<\begin{smallmatrix}NH_2 . HSCN\\ NH_2 . HSCN\end{smallmatrix}$, are produced. On heating these to 120° we discover that the orthodiamines are changed to *cyclic sulphureas*, $C_6H_4<\begin{smallmatrix}NH\\ NH\end{smallmatrix}>CS$. These are not altered by digestion with an alkaline lead-solution (not desulphurized); while the derivatives, obtained from the *meta*- and *para*-diamines, are immediately blackened by the alkaline lead-solution (Reaction of Lellmann, B. **18**, R. 326).

4. The diamines unite in a similar manner with the *mustard oils*. If these products be fused, those from the *ortho-diamines* decompose into cyclic phenylenesulphurea and dialkylsulphureas; the fused mass instantly becomes crystalline. The *meta*-diamine derivatives melt without decomposition, while those of the *para*-, after fusion, are completely broken up (B. **18**, R. 327, and **19**, 808).

5. The o-diamines show a series of other condensation reactions, which have been tabulated above, and as the m- and p-diamines behave differently in these transpositions, they will answer for the distinction of the o-derivatives from the other two classes. The behavior toward *phenanthraquinone* is used for the detection of the o-diamines. A more delicate test is that with *croconic acid* (B. **19**, 2727). Both tests are based upon the formation of quinoxaline derivatives

Triamines.—The three triamidobenzenes possible theoretically are known, although the symmetrical body only in the form of its salts.

The *adjacent* (1,2,3) is obtained from triamidobenzoic acid (from chrysanisic acid). When pure it melts at 103° and boils at 330° (A. **163**, 23). The *unsymmetrical* (1,2,4), melting at 132° and boiling at 340°, is obtained by the decomposition of chrysoïdine (B. **10**, 659; **15**, 2196), or diamidoazobenzene (p. 116), and from compounding nitroamido-derivatives (B. **19**, 1253). When oxidized by air it changes to a eurhodine dyestuff (B. **22**, 856). [$1CH_3$,2,3,4]-*Triamidotoluene* (B. **14**, 2657). *a*-**Diamidodimethyl Aniline** boils at 178° (22 mm.); see B. **29**, 1053.

Tetramines.—v-,[1,2,3,4]-Tetra-amidobenzene is obtained by the reduction of diquinoyl tetroxime (B. **22**, 1649). The *symmetrical* (1,2,4,5) variety is formed by the reduction of dinitro-m-phenylenediamine. It exhibits all the reactions of the ortho- and para-diamines (B. **22**, 440).

Pentamines.—Penta-amidobenzene, from trinitro-m-phenylenediamine, is very unstable on exposure to the air.

Penta-amidotoluene, $CH_3 . C_6(NH_2)_5$, is formed from trinitro-s-toluylene diamine (B. **26**, 2304).

As the number of amido-groups increases the polyamines become more unstable.

6. PHENYL-NITROSAMINES.

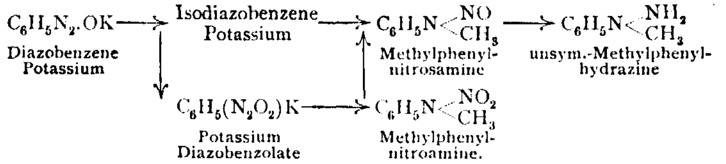
Nitroso-compounds are obtained when potassium nitrite acts upon the hydrochlorides of secondary aromatic bases. This procedure is similar to that employed with the aliphatic nitrosamines. It is a reaction which can be used to distinguish and separate secondary from primary and tertiary bases, as the nitrosamines are precipitated as oils from the acid solution of a mixture of bases. The phenyl-nitrosamines in alcoholic or ethereal solution, when treated with hydrochloric acid gas, pass into p-nitroso-anilines (p. 94):

$$C_6H_5N<\begin{smallmatrix}CH_3\\ NO\end{smallmatrix} \longrightarrow NO[4]C_6H_4[1]NHCH_3$$

Methylphenyl-nitrosamine — p-Nitrosomonomethyl Aniline.

They change into hydrazines upon reduction, or break down into ammonia and the original secondary bases. They are volatile with steam (B. 10, 329; 22, 1006; A. 190, 151) and decompose upon distillation.

The nitrosamines are not only intimately related to the secondary amines and hydrazines, but also to the diazo-compounds. Diazobenzene potassium may be readily rearranged into isodiazobenzene potassium, which yields phenylmethyl-nitrosamine with methyl iodide. unsym.-Phenylmethyl-hydrazine results from the reduction of phenylmethyl-nitrosamine. Potassium diazobenzolate is formed by the oxidation of isodiazobenzene potassium. The latter and methyl iodide combine to methyl a-diazobenzolate, the phenylmethyl-nitramine, which can be reduced to phenylmethyl-nitrosamine and unsym.-phenylmethyl-hydrazine. These relations are indicated in the following diagram:



Phenylmethyl-nitrosamine, $C_6H_5N(CH_3)NO$, melts at 12–15° (B. 27, 365 Anm.). The methyl group is replaced by potassium when the substance is fused with caustic potash; potassium isodiazobenzene results.

Phenylethyl-nitrosamine, $C_6H_5N(C_2H_5)NO$, is a yellow oil with an odor like that of bitter almond oil (B. 7, 218).

Diphenyl-nitrosamine, $(C_6H_5)_2NNO$, melting at 66°, consists of pale yellow plates. It dissolves in concentrated sulphuric acid with a dark-blue color.

Nitrosoanilides.—Nitrosoformanilide, $C_6H_5N(NO)CHO$, melting at 39°, is produced when nitrous acid acts upon formanilide dissolved in glacial acetic acid. **Nitroso-acetanilide**, melting at 40°, recalls in its deportment the diazo-compounds. It is saponified by alkali to potassium diazobenzene. It yields diphenyl, with liberation of nitrogen, when it is treated with benzene. Potassium sulphite changes it to benzene diazosulphonic acid and phenylhydrazine disulphonic acid (p. 103) (B. 30, 366).

7. PHENYLNITRAMINES.

Diazobenzene Acid, *Nitranilide*, $C_6H_5NH.NO_2$, or $C_6H_5N:N.OOH$, colorless crystals melting at 46°, is formed:

(1) On oxidizing diazo- and isodiazo-benzene potassium with potassium ferricyanide (B. 27, 2602), or with potassium permanganate (B. 28, R. 82); (2) by the nitration of aniline with nitrogen pentoxide (B. 27, 584; compare 29, 1015); (3) by decomposing diazobenzene perbromide with alkalies (B. 28, R. 31), together with nitrosobenzene (B. 27, 1273); (4) from nitryl chloride and aniline (B. 27, 668); (5) from aniline nitrate and acetic anhydride through the loss of water, just as in the case of acetanilide and aniline acetate. A series of other diazobenzene acids has been prepared by methods (2) and (5).

Properties and Behavior.—Diazobenzene acid is rearranged by light, by heat, and by contact with mineral acids into a mixture of o- and p-nitraniline (p. 93), with which it is isomeric. Sodium amalgam reduces it to isodiazobenzene sodium, and the latter with ease to phenylhydrazine (B. 27, 1181). Zinc and acetic acid convert it into diazobenzene. It forms salts. The *potassium salt*, $C_6H_5N_2O_2K$, and *sodium salt*, consist of white, glistening leaflets. Methyl iodide converts the sodium salt into the a-methyl ester, **Phenylmethylnitramine**, $C_6H_5N<{CH_3 \atop NO_2}$, melting at 39°. The latter is changed by sulphuric acid to o- and p-nitromethyl aniline. It is converted into methyl aniline when heated with caustic potash. It can be reduced to methylphenyl-nitrosamine, unsym.-methylphenyl-hydrazine and monomethyl aniline. Methyl iodide converts the *silver salt* into *β-diazobenzene methyl ester*, $C_6H_5N:NO.O.CH_3$, a yellow-brown oil with an odor like heliotrope (B. 27, 359).

Homologous Diazobenzene Acids.—**o-Diazotoluene Acid** is a colorless oil. **p-Diazotoluene Acid** melts at 52°. **Diazopseudocumene Acid** melts at 87°. o-, m-, and **p-Nitrodiazobenzene Acids** melt at 65°, 86°, and 111° (B. **28**, 399). **Dinitro-p-tolylmethylnitramine**, $(NO_2)_2C_6H_2(CH_3).N(CH_3)NO_2$, melting at 138°, has been prepared by the action of nitric acid upon dimethyl-p-toluidine (B. **29**, 1015).

8. DIAZO-COMPOUNDS.

The aromatic diazo-derivatives, because of their ready conversion into the most varied substitution products of the aromatic hydrocarbons, and as intermediate steps in the formation of azo-dyes, are equally important both from a scientific and technical standpoint.

The behavior of the primary aliphatic amines toward nitrous acid was particularly emphasized in connection with them. As is known, the amido-group can, by this means, be replaced by hydroxyl; it is a change corresponding to that of ammonia itself by nitrous acid into nitrogen and water:

$$NH_3 + NOOH = H_2O + N_2 + H_2O$$
$$C_2H_5NH_2 + NOOH = C_2H_5OH + N_2 + H_2O.$$

Among the nitrogen-containing derivatives of the aldehydo-acids we observed a body, in the reaction-product, resulting from nitrous acid and glycocoll ester, in which the group — N = N — had joined itself to carbon. This substance has been termed *diazoacetic ester*, produced according to the equation:

$$CO_2C_2H_5.CH_2.NH_2 + NOOH = CO_2C_2H_5.CH(N_2) + 2H_2O.$$

The moderated action of nitrous acid upon the salts of aromatic primary amines is analogous to its action upon aliphatic α-amido-acid esters. It was, however, observed long before the latter. When nitrous acid acts upon the aqueous solution of salts of primary aromatic amines without taking care to cool the mixture, there follows, as in the case of the aliphatic amines, a replacement of the amido-group by hydroxyl:

$$C_6H_5NH_2HCl + NOOH = C_6H_5OH + N_2 + H_2O + HCl.$$

Upon cooling the solution, however, the three hydrogen atoms will be replaced by a nitrogen atom, thus:

$$C_6H_5NH_3Cl + NOOH = \underset{\text{Diazobenzene Chloride}}{C_6H_5NCl \equiv N} + 2H_2O$$
$$C_6H_5NH_3ONO_2 + NOOH = \underset{\text{Diazobenzene Nitrate}}{C_6H_5N(O.NO_2) \equiv N} + 2H_2O$$
$$C_6H_5NH_3OSO_3H + NOOH = \underset{\text{Diazobenzene Sulphate.}}{C_6H_5N(O.SO_3H) \equiv N} + 2H_2O$$

These aromatic diazo-bodies differ from the aliphatic in that the bivalent group N_2 is linked not with *both*, but only with one affinity to the carbon atom. The second affinity is joined to another univalent radical. Bodies of this class, when boiled with water, yield oxy-compounds:

$$CO_2C_2H_5.CHN_2 + H_2O = CO_2C_2H_5.CH_2OH + N_2$$
$$C_6H_5N_2Cl + H_2O = C_6H_5OH + HCl + N_2.$$

Formation of Diazobenzenes.—(1*a*) Gaseous nitrous acid, made by digesting arsenious acid with nitric acid, is conducted into a paste of the salt to be diazotized. The mixture is cooled all the while with ice. The solution of the diazo-compound is precipitated by a mixture of alcohol and ether. (1*b*) Add acid to the cooled solution of the salt to be diazotized sufficient (B. **8**, 1073; **25**, 1974 Anm.; **29**, R. 1158) to liberate the nitrous acid from sodium or potassium nitrite, the well-cooled solution of which is gradually introduced into the acidified liquid:

$$C_6H_5NH_2 . HCl + HCl + NO_2K = C_6H_5N_2Cl + 2H_2O + KCl.$$

(2) As the diazobenzene salts are more freely soluble in water than in alcohol, in order to obtain solid diazo-salts the diazotizing, where practicable, should be made with alkyl nitrites (1, 144) dissolved in alcohol (15 parts of aniline, 150 parts of absolute alcohol, 20 parts of sulphuric acid, and 20 parts of amyl nitrite; B. **23**, 2994; **28**, 2048).

Sometimes a peculiar migration of the diazo-groups takes place on mixing the solution of an aniline salt with a diazo-salt solution. Thus, toluene diazochlorides and nitranilines (B. **29**, 287) arise from nitrodiazobenzene chlorides and toluidines:

$$NO_2C_6H_4N_2Cl + C_6H_4(CH_3)NH_2 = NO_2 . C_6H_4 . NH_2 + C_6H_4(CH_3)N_2Cl.$$

(3) Another procedure, occasionally applicable in diazotizing, consists in letting zinc-dust and hydrochloric acid act upon the nitrate of the diazo-derivative (B. **16**, 3080):

$$C_6H_5 . NH_2 . NO_3H + Zn + 3HCl = C_6H_5 . N_2Cl + ZnCl_2 + 3H_2O.$$

(4) By the action of hydroxylamine upon the nitrosobenzenes:

$$C_6H_5NO + H_2NOH = C_6H_5N : NOH + H_2O.$$

(5) Diazobenzene nitrate is precipitated upon conducting nitric oxide into a chloroform solution of nitrosobenzene (B. **30**, 512):

$$C_6H_5NO + 2NO = C_6H_5N_2NO_3.$$

(6) By the saponification of nitrosoacetanilide with caustic alkali (p. 98).

(7) By the action of mercuric oxide upon the phenylhydrazines (p. 120).

(8) By allowing thionyl chloride, acetyl chloride, and other acid chlorides to act upon thionyl phenylhydrazone. The latter reacts in the form of diazobenzene-sulphoxyl, $C_6H_5N = NS(OH)$ (B. **270**, 116):

$$C_6H_5N = NSOH + CH_3COCl = C_6H_5N_2Cl + S + CH_3 . CO_2H.$$

Properties.—The acid salts of the diazo-compounds are mostly crystalline, colorless bodies, which speedily brown on exposure to the air. They are readily soluble in water, slightly in alcohol, and are precipitated from the latter solution by ether. Consult B. **28**, 1734, 2020, for their electric conductivity and cryoscopic behavior. They are generally very unstable (B. **24**, 324) and decompose with a violent explosion when they are heated or struck a blow.

The diazo-derivatives are very reactive, and enter numerous, readily occurring reactions, in which nitrogen is liberated, and the diazo-group in the benzene nucleus directly replaced by halogens, hydrogen, hydroxyl, and other groups.

History and Constitution.—The diazo-compounds were discovered at the close of the '50s by Peter Griess (A. 137, 39), who regarded their salts as additions of $C_6H_4N_2$ and acids, *e. g.*, HCl. Kekulé demonstrated that the azo-group only replaced one hydrogen of benzene, and held on the opposite side the radical of the acid, *e. g.*, $C_6H_5 - N = N . Cl$ (Z. f. Ch. N. F. (1866) 2, 308; Chemie der Benzolderivate 1, 223). Blomstrand, A. Strecker, and E. Erlenmeyer, Sr., however, viewed the diazo-salts as ammonium salts, *e. g.*, $C_6H_5N(Cl) \equiv N$.

Proof of the fact that the azo group N_2 replaces *one* benzene hydrogen atom is supposed to be found in the existence of such bodies as tetrabrombenzene-sulphanil-diazide, $C_6Br_4<^{N_2}_{SO_3}>$(B. 10, 1537). The relations of the *diazobenzene salts* to the *hydrazines*, (E. Fischer, A. 190, 100), and to the mixed azo-compounds argued in favor of Kekulé's representation.

In recent years Blomstrand's formula has been accepted for the acid salts of the diazo-bodies (B. 29, R. 93, 783). Comparative studies of the cryoscopic behavior and the electric conductivity of diazo-salt solutions on the one side, and ammonium and alkali salts on the other (B. 28, 1734, 2020), have contributed to this assumption. The diazo-salts are compared to the quaternary ammonium salts:

$$\underset{\displaystyle Cl}{C_6H_5\overset{|}{N}:N} \qquad\qquad \underset{\displaystyle Cl}{C_6H_5\overset{|}{N} : (CH_3)_3},$$

and therefore are termed diazonium salts. From a chemical standpoint this view would indicate, among other things, the power of the diazonium haloids to form additive compounds with the halogens (p. 102)—a property which they would hold in common with quaternary ammonium halides (1, 168), as well as with certain alkali metals—*e. g.*, caesium, rubidium. This formula also permits of the easy conversion of the aniline salts by means of nitrous acid into diazo-salts, without being compelled to assume, as is necessary in the Kekulé formula, the migration of the acid residue from the aniline nitrogen to the nitrogen atom which has but recently entered:

$$\underset{\displaystyle Cl}{C_6H_5\overset{|}{N}H_3} + NO_2H = \underset{\displaystyle Cl}{C_6H_5\overset{|}{N} \equiv N} + 2H_2O.$$

The hydrates corresponding to the diazonium salts are very unstable; they, however, yield metallic salts, $C_6H_5N_2OMe$, which can be handled. The *diazoalkali salts* are partially rearranged at the ordinary temperature, and partly on heating (B. 29, 455) into *isodiazo-salts*. The latter differ from the former in that they do not combine, or at least with difficulty, with aromatic amines or phenols to form dyes (Schraube and Schmidt, B. 27, 514). Inasmuch as these isodiazoalkali salts yield phenylmethyl-nitrosamines with methyl iodide (p. 98), while the normal diazo-salts form normal diazo-methyl esters with methyl alcohol, the nitrosamine formula—*e. g.*, $C_6H_5NK . NO$—was ascribed to the former. This view has not held true (B. 27, 1707), because, in acidylating, for example, with acid chlorides or anhydrides and sodium hydroxide, it is exactly the normal salts which afford nitroso-acid anilides, while the iso-salts are but slightly attacked by these reagents, and are in part reconverted into the normal salts (B. 30, 211). Bamberger viewed the normal diazo-bodies as derivatives of the real diazonium hydroxide, $C_6H_5N(OH):N$, and left the Kekulé formula, $C_6H_5N:NOH$, for the iso-derivatives, as they were directly produced from nitrosobenzenes and hydroxylamine (p. 100). In the opinion of Hantzsch the isomerism of the diazobenzene alkali salts, in case of structural identity, is influenced by stereoisomerism (see benzaldoximes), corresponding to the following representations:

$$\begin{array}{cc} C_6H_5N & C_6H_5N \\ \| & \| \\ KON & N.OK \end{array}$$

Syn-diazobenzene Potassium   **Anti-diazobenzene Potassium.**

This last view allows of three classes of diazo-compounds: diazonium salts, syn- and

anti-diazo-compounds. The second and third are formed from and by a rearrangement of the first.

Isomeric series of diazobenzene sulphonic acids and diazocyanides have also been discovered.

1. **Diazonium Salts.—Diazobenzene Chloride**, $C_6H_5NCl \equiv N$, colorless needles (B. **23**, 2996; **28**, 2053). The *platinum salt*, $[C_6H_5N_2Cl]_2PtCl_4$, consists of yellow prisms. The *gold salt*, $C_6H_5N_2Cl . AuCl_3$ (A. **137**, 52). *Mercury salt*, $C_6H_5N_2Cl . HgCl_2$, consists of white needles, decomposing at 122°. *Diazobenzene Bromide*, $C_6H_5 . N_2Br$, separates in white laminæ, if bromine be added to the ethereal solution of diazo-amidobenzene. Tribrom-aniline remains in solution. *Diazobenzene Bromide Cuprous Bromide*, $C_6H_5N_2Br . Cu_2Br_2$, consisting of reddish-yellow needles, is decomposed by water into cuprous bromide, nitrogen, and brombenzene (p. 105) (B. **28**, 1741).

Diazoperhalides.—The diazonium halides readily add two halogen atoms. The trichloride of the ten combinations possible with the halogens, chlorine, bromine, and iodine, is the only one that has not been prepared. It may be remarked that the compound $C_6H_5N_2BrICl$ can be both prepared as well from the chloride and BrI as from the bromide and Cl I (B. **28**, 2754).

Diazobenzene Perbromide, $C_6H_5 . N_2Br_3$, is precipitated from the aqueous solution of diazobenzene nitrate or sulphate, by bromine in HBr-acid or NaBr. It is a dark-brown oil, which quickly becomes crystalline. It is insoluble in water and ether, and crystallizes from cold alcohol in yellow laminæ. Continued washing with ether converts it into diazobenzene bromide. It is changed by aqueous ammonia to diazobenzene imide (p. 111). Alkalies decompose it into nitrosobenzene and potassium diazobenzene (p. 98). Boiling alcohol converts it into brombenzene (p. 105).

Diazobenzene Nitrate, $C_6H_5N_2O . NO_2$, consists of long, colorless needles which explode with greater violence than fulminating mercury or nitrogen iodide when they are gently heated, struck, or subjected to pressure.

Diazobenzene Sulphate, $C_6H_5 . N_2 . SO_4H$, consists of colorless needles or prisms, which dissolve readily in water. It explodes at 100°. It is prepared either by diazotizing aniline sulphate or by allowing sulphuric acid to act upon diazobenzene nitrate (B. **28**, 2049).

Oxalate (B. **28**, 2059).

Carbonate, Nitrite, Acetate (B. **28**, 1741).

Diazobenzene Sulphocyanide, $C_6H_5N_2 . SCN$, is a yellow, very explosive mass, obtained from diazobenzene chloride and potassium sulphocyanide. p-*Chlordiazobenzene Sulphocyanide*, $Cl[4]C_6H_4N_2 . SCN$, rearranges itself with ease into p-sulphocyan-diazobenzene chloride, $CNS[4]C_6H_4N_2Cl$ (B. **29**, 947).

p-*Phenylenebisdiazo-chloride*, $C_6H_4(N_2Cl)_2$, consists of yellow-colored, very explosive needles (B. **30**, 92).

2. **Normal Diazohydrates** are not known in a free state. In attempting to separate them by acids from their potassium salts, yellow-colored, exceedingly explosive and unstable precipitates are obtained under certain conditions. These appear not to be hydrates, but *anhydrides—e. g.*, *diazobenzene anhydride*, $[C_6H_5N_2]_2O$; p-*chlordiazobenzene anhydride*, $[ClC_6H_4N_2]_2O$. These bodies redissolve in acids to diazonium salts, in alkalies to diazometallic salts, in ammonia to bisdiazoamido-bodies, and in anilines to diazoamido-compounds (B. **29**, 451).

Normal *Diazobenzene Potassium*, $C_6H_5N_2OK$, is produced on introducing a saturated aqueous solution of diazobenzene chloride into excessive and highly concentrated caustic potash (B. **29**, 461). It forms white, pearly leaflets which can be quantitatively reconverted into diazobenzene chloride. It yields diazo-esters in the cold with alcohols (B. **29**, 488): see B. **30**, 339 for the reduction of potassium diazobenzene to phenylhydrazine. When alkaline diazobenzene solutions are oxidized with potassium ferricyanide or potassium permanganate the principal product is *diazobenzene acid* (p. 98), together with a little nitrosobenzene (p. 66), nitrobenzene (p. 70), azobenzene (p. 112), and diphenyl. Benzoyl chloride and sodium hydroxide change normal potassium diazobenzene into nitrosobenzanilide, $C_6H_5N(NO) . CO . C_6H_5$ (B. **30**, 214). Salts of the heavy metals with diazobenzene are obtained by the precipitation of solutions of potassium diazobenzene with metallic salts (B. **23**, 3035; **28**, 226).

Diazobenzene Methyl Ether, $C_6H_5N_2 . OCH_3$, isomeric with methylphenyl-nitrosamine

(p. 98), is obtained from normal or iso-diazobenzene-silver and methyl iodide, as well as from diazobenzene potassium and methyl alcohol. It is a yellow, volatile oil, rapidly turning dark in color, possessing a penetrating, stupefying odor, and decomposing shortly after its liberation. Boiling dilute sulphuric acid decomposes it into nitrogen, methyl alcohol, and phenol (B. **28**, 227). o- and p-*Nitrodiazobenzene Methyl Ether*, NO_2.$C_6H_4N_2$.OCH_3 (B. **28**, 236). *Di*-p-*nitrophenyldiazo-sulphide*, $[NO_2[4]C_6H_4N_2]_2S$, is precipitated as an egg yellow, very explosive mass, on adding hydrogen sulphide to a neutral solution of the diazo-chloride. With benzene it forms nitrodiphenyl, nitrogen, and sulphur; di-p-nitrodiphenyl disulphide is formed simultaneously. In an acid solution with an excess of hydrogen sulphide there is produced, along with the diazosulphide, p-*nitrophenyldiazomercaptan hydrosulphide*, NO_2.$C_6H_4N_2SH$.SH_2, consisting of red, brilliant, metallic-looking needles, which dissolve with a deep-red color in the alkalies. They decompose, when fused, with the formation of nitrophenylhydrazine, nitraniline, sulphur, and dinitrophenyl disulphide. Non-explosive *Di*-p-*nitrophenyldiazodisulphide*, $[NO_2C_6H_4N_2]_2S_2$, is finally the third product in the action of hydrogen sulphide. It is insoluble in alkali. It consists of sulphur-yellow needles, soluble in acetone (B. **29**, 272). See thiophenol for diazobenzene thiophenyl ether.

3. **Isodiazohydrates** are liberated from their potassium salts by acetic acid. They are very easily decomposed. Those of benzene and toluene are colorless oils. p-*Nitroisodiazobenzene hydrate*, NO_2.$C_6H_4N_2OH$ (B. **29**, 1383), has been analyzed.

Potassium Isodiazobenzene, $C_6H_5N_2OK$, is formed on digesting potassium diazobenzene for a brief period at 130–135° with concentrated caustic potash, and when fused, caustic potash acts upon phenylmethyl-nitrosamine (p. 98), into which it returns upon treatment with methyl iodide (B. **27**, 514, 672, 680). Sodium amalgam reduces it with ease to phenylhydrazine (B. **29**, 473; **30**, 339). *Potassium Iso*-p *diazotoluene* results when its isomeride lies exposed to the air (B. **29**, 1385). *Iso*-p-*nitrodiazobenzene sodium*, $C_6H_4(NO_2)N_2ONa + 2H_2O$, yields nitrophenylmethyl-nitrosamine with methyl iodide, whereas the *silver salt* forms the corresponding diazo-ester (B. **29**, 1384).

Diazobenzene Sulphonic Acid, *Benzene-azosulphonic Acid*, $C_6H_5N_2SO_3H$, is very decomposable (B. **30**, 75). Its potassium salt is produced upon introducing diazobenzene nitrate into a cold, neutral, or feebly alkaline solution of dipotassium sulphite; the liquid solidifies to a yellow, crystalline mass. Under other conditions a more easily decomposable, orange-colored salt is formed (B. **27**, 1715, 2930). For the sensitivity of the diazobenzene sulphonates to light and their application in photography consult B. **23**, 3131. Monopotassium sulphite reduces diazobenzene nitrate to potassium phenylhydrazine sulphonate (p. 119), which mercuric oxide oxidizes to potassium diazobenzene sulphonate (B. **27**, 1245).

p-Nitrodiazobenzene nitrate and one molecule of K_2SO_3 yield *potassium* p-*nitrodiazobenzene sulphonate*, which also appears to exist in two forms. The acid crystallizes with four molecules of water in ruby-red prisms (B. **30**, 90). On using two molecules of potassium sulphite the product is *potassium* p-*Nitrophenylhydrazine disulphonate*, $C_6H_4(NO_2)N(SO_3K)NH$.SO_3K (p. 125) (B. **29**, 1829). p-*Chlor*- and p-*Brombenzene Diazosulphonic Acid* (B. **30**, 75).

The diazonium salts and benzene sulphinic acid combine to *Benzene diazosulphones*, $C_6H_5N_2SO_2C_6H_5$, which are resolved by hydrochloric acid into diazonium chlorides and sulphinic acids (B. **30**, 312).

Diazobenzene Cyanide, $C_6H_5N_2CN$, appears as an unstable oil, on adding a potassium cyanide solution to the solution of a diazobenzene salt. If, however, the reverse be done—the diazo-salt be added to the potassium cyanide solution—a *prussic acid additive product*, $C_6H_5N_2CN$.HCN, will separate as a yellow precipitate, melting at 70°. *Benzenediazocarbonamide*, phenylazocarbamide, $C_6H_5N : NCONH_2$, results from the oxidation of phenylsemicarbazide (p. 127) (J. ch. Soc., 1895, I, p. 1067; B. **28**, 1925, 2599). It consists of reddish-yellow needles, melting at 114°. The *anilide*, $C_6H_5N_2$-$CONHC_6H_5$, from diphenylsemicarbazide (B. **29**, 1691), melts at 122°.

Two isomerides have been obtained from p-chlor- and p-nitrodiazobenzene cyanide, and in each instance the one body is unstable and the other stable. The unstable, low-melting modifications only form at lower temperatures, decompose easily, especially in contact with copper powder (p. 105), give up nitrogen with the formation of benzene cyanides, form azo-dyes with aromatic amines or phenols, and change rapidly, particu-

larly in alcoholic solution, into the stable isomerides. Unstable p-*chlor-* and p-*nitrodiazobenzene cyanide*, melt at 28° and 29°; stable p-*chlor-* and p-*nitrodiazobenzene cyanide* melt at 106° and 86°. The stable cyanides unite to diazocarbonamides with water, and with alcohols to *imido ethers*, from which the potassium salts of the corresponding diazobenzene carboxylic acids can be obtained by saponification. The acids themselves are very decomposable (B. **28**, 670, 2072). *Tribromphenylazocarboxylic Acid*, $C_6H_2Br_3 . N_2 . COOH$, has been obtained from its amide, the oxidation product of tribromphenylsemicarbazide (B. **28**, 1929).

The Most Important Decompositions of the Diazobenzene Salts.—The decompositions of the diazo-salts in which nitrogen is evolved and atoms of other non-metals or atomic groups enter and take its place are of the greatest importance for the genetic relations of very many of the most varied di- and polysubstitution products of benzene and its homologues (p. 38).

(1) *Replacement of the Diazo-group by Hydrogen*:

(*a*) If the salts be boiled with strong alcohol, then hydrogen will enter for the diazo-group, and hydrocarbons result. The alcohol is oxidized to aldehyde (A. **137**, 69; **217**, 189; B. **9**, 899):

$$C_6H_5 . N_2 \; HSO_4 + C_2H_6O = C_6H_6 + N_2 + SO_4H_2 + C_2H_4O.$$

It has occurred upon boiling with alcohol that the diazo-group was not replaced by hydrogen, but by oxy-ethyl ($O . C_2H_5$), with the production of phenol ethers (B. **17**, 1917; **18**, 65; **26**, R. 547). If the dry diazo-salt be decomposed with alcohol, phenol ethers are the chief products (B. **21**, R. 99; **22**, R. 657).

(*b*) The replacement of the diazo group by hydrogen is sometimes effected by its conversion into the hydrazine derivative and then boiling this with copper sulphate or ferric chloride (see phenylhydrazine). The reaction taking place on boiling the diazo-chlorides with a stannous chloride solution is, in all probability, dependent upon the intermediate formation of hydrazines (B. **22**, R. 741):

$$C_6H_4(C_4H_9) . N_2Cl + SnCl_2 + H_2O = C_6H_5(C_4H_9) + N_2 + SnOCl_2 + HCl.$$

(*c*) An analogous procedure for the replacement of the diazo-group by hydrogen consists in dissolving the diazo-compound in caustic soda and adding a solution of stannous oxide in sodium hydroxide (B. **22**, 587). Diphenyl derivatives frequently appear as secondary products.

(*d*) The diazides of sulphonic acids can be boiled with copper powder and formic acid (B. **23**, 1632).

(2) *Replacement of the Diazo-group by Halogens*:

(*a*) The diazobenzene salts are treated with haloid acids. Hydriodic acid of the four acids of this class reacts most readily:

$$C_6H_5N_2 . OSO_3H + HI = C_6H_5I + N_2 + SO_4H_2.$$

The haloid acids are frequently applied in glacial acetic acid solution.

The hydrobromides or hydroiodides of the bases can also be treated with nitric acid.

(*b*) Concentrated haloid acids are allowed to act upon the diazo-amido-derivatives (p. 109). This reaction is especially recommended for the preparation of fluor- or chlor-derivatives (B. **21**, R. 97):

$$C_6H_5N = N . NH . C_6H_5 + 2HF = C_6H_5F + N_2 + FH . NH_2 . C_6H_5.$$

(*c*) Chlor- and brom-derivatives are formed, if the $PtCl_4$- and $PtBr_4$-double salts are heated alone; or, what is better, with dry soda or salt:

$$(C_6H_5 . N_2Cl)_2 . PtCl_4 = 2C_6H_5Cl + N_2 + 2Cl_2 + Pt.$$

(*d*) When the diazo-perbromides are boiled with alcohol (the latter is oxidized to aldehyde), brombenzenes are formed:

$$C_6H_5 . N_2 . Br_3 + CH_3CH_2OH = C_6H_5Br + N_2 + 2HBr + CH_3 . CHO.$$

The reactions indicated under *a*, *b*, *c*, and *d* were all observed by P. Griess. Another reaction belongs in this group: it was discovered by Sandmeyer (B. **17**, 2650; **23**, 1880), and is capable of far greater generalization. It is based upon the fact that diazo-salts are decomposed by cuprous salts:

(*e*) When cuprous chloride is added to an aqueous solution of diazobenzene chloride, an additive product, $C_6H_5N_2Cl . Cu_2Cl_2$, is formed at first, but upon the application of heat this decomposes into C_6H_5Cl (B. **19**, 810; **23**, 1628; A. **272**, 141):

$$C_6H_5N_2Cl(Cu_2Cl_2) = C_6H_5Cl + N_2 + Cu_2Cl_2.$$

Cuprous bromide and cuprous iodide act similarly upon the corresponding diazobenzene salts.

A modification of the method consists in treating the diazo-derivatives in the presence of hydrochloric, hydrobromic, or hydriodic acid with copper powder (B. **23**, 1218; **25**, 1091 Anm.).

(3) *Replacement of the Diazo-group by Hydroxyl.*—When the salts (sulphates are best) are boiled with water, the diazo-group will be replaced by hydroxyl:

$$C_6H_5 . N_2 . Br + H_2O = C_6H_5 . OH + N_2 + HBr$$
$$C_6H_5 . N_2 . NO_3 + H_2O = C_6H_5 . OH + N_2 + NO_3H$$
$$C_6H_5N_2SO_4H + H_2O = C_6H_5OH + N_2 + SO_4H_2.$$

Nitro-phenols appear as side products in the decomposition of the diazonitrates. It was mentioned upon p. 104 that in the action of alcohol upon diazo-salts alkyl phenol ethers are formed, together with the hydrocarbons; similar products are observed when phenol (B. **23**, 3705), glacial acetic acid (B. **21**, R. 889), and acetic anhydride (A. **235**, 234) are used.

(4) *Replacement of the Diazo-group by the Sulphydrate Group.*—On digesting the diazide of sulphanilic acid (see this), a cyclic diazo salt, with alcoholic potassium sulphide, the potassium salt of p-thiophenolsulphonic acid will be produced (B. **20**, 350):

$$C_6H_4 < \left\{ \begin{matrix} [1]N_2 \\ [4]SO_3 \end{matrix} \right> + K_2S = C_6H_4 < \left\{ \begin{matrix} [1]SK \\ [4]SO_3K \end{matrix} \right. + N_2.$$

In the same manner, when mercaptan acts upon diazobenzenesulphonic acid, a compound results which, upon standing or warming, decomposes into thiophenolethylether-p-sulphonic acid:

$$C_6H_4 < \begin{matrix} N_2 \\ SO_3 \end{matrix} > \longrightarrow C_6H_4 < \begin{matrix} N_2SC_2H_5 \\ SO_3H \end{matrix} \longrightarrow C_6H_4 < \begin{matrix} SC_2H_5 \\ SO_3H \end{matrix}.$$

The xanthates yield aromatic xanthogenic esters,—*e. g.*, $C_6H_5S . CSOC_2H_5$,—which, upon saponification, yield thiophenols (J. pr. Ch. [2] **41**, 184). The formation of di-p-nitrophenyldisulphide by the decomposition of the corresponding diazosulphide and mercaptan has already received mention (p. 103).

(5) *Replacement of the Diazo-group by the Nitro-group.*—This may be accomplished by adding the diazobenzene nitrite solution to freshly precipitated cuprous oxide (B. **20**, 1495; **23**, 1630).

(6) *Replacement of the Diazo group by the Cyanogen Group.*—This reaction connects by easy stages the nitroamidobenzenes with the nitrobenzoic acids, and the latter with the phthalic acids. The importance of this fact has received mention (p. 38). Add the diazobenzene chloride solution to a copper sulphate solution mixed with potassium cyanide (B. **20**, 1495; **23**, 1630) (compare p. 103):

$$C_6H_5N_2CN = C_6H_5CN + N_2.$$

(7) Sulphocyanides (*Rhodanides*) result when the diazo-salts are boiled with potassium and cuprous sulphocyanides (B. **23**, 770).

(8) When a solution of diazobenzene sulphate is mixed with potassium cyanate and reduced copper is then added (B. **25**, 1086), phenylisocyanide or *carbanile* will result (p. 89).

(9) *Formation of Diphenyl Compounds from Diazo-derivatives.*—Diphenyl derivatives frequently appear as side products in the treatment of diazo-bodies with reducing agents —*e. g.*, stannous chloride (B. **18**, 965), alcohol, and reduced copper (B. **23**, 1226), alcohol alone or sodium ethylate (B. **28**, R. 389)—as well as in the action of water, of phenol (B **23**, 3705), and of potassium ferricyanide (B. **26**, 471). Into aromatic hydrocarbons and heterocyclic compounds—*e. g.*, thiophene, pyridine, and quinoline—diazobenzene chloride introduces the phenyl group. This occurs very easily in the presence of aluminium chloride (B. **26**, 1994):

$$C_6H_5N_2Cl + C_6H_6 \xrightarrow{Al_2Cl_6} C_6H_5C_6H_5 + N_2 + HCl.$$

The diazo-residue in the diazo-oxides, diazo-sulphides, and isodiazohydrates is readily replaced by cyclic residues (B. **28**, 404; **29**, 165, 274, 452):

$$[NO_2 . C_6H_4N_2]_2S + 2C_6H_6 = 2NO_2 . C_6H_4 . C_6H_5 + N_2 + H_2S$$

$$C_6H_5N_2OH + \underset{\text{Pyridine.}}{C_5H_5N} = C_6H_5 . C_5H_4N + N_2 + H_2O.$$

Other Reactions of Diazo-derivatives, in which nitrogen is not set free.

1. Phenylhydrazines are produced in the reduction of diazo-salts (p. 119).

2. When diazo-compounds are oxidized in alkaline solution, they are converted into nitrosobenzene (p. 70) and phenylnitroamine or diazobenzene acid (p. 98).

3. The behavior of diazo-bodies toward ammonia, alkylamines, aniline, and related bases, when diazoimido- (p. 110), diazoamido- (p. 107), and mixed azo-derivatives arise, is worthy of special note. These very important reactions will be given in detail, with the individual classes.

4. Hydrazones result when diazobenzene in alkaline solution acts upon bodies containing the group $CH_2 . CO$ (p. 121). The primarily formed hydrazones often rearrange themselves with additional quantities of the diazobenzene salt into *formazyl* derivatives, which belong to the class of amidines (I, 270) (B. **27**, 147, 320, 1679; **29**, 1386).

9. DIAZOAMIDO-COMPOUNDS. 10. DISDIAZOAMIDO-COMPOUNDS.

The *diazoamido-compounds* are derived from the unknown hydride $NH = N - NH_2$, in which the hydrogen of the imide group is replaced by an

aromatic residue—*e. g.*, phenyl, tolyl, etc.—and the hydrogen of the amido-group by aliphatic or aromatic residues: ***mixed and true aromatic diazoamido-compounds.*** The ***disdiazoamido bodies*** are also derivatives of an unknown nitrogen hydride, $NH = N - NH - N = NH$.

Formation of Diazoamido-derivatives.—They result from the transposition of primary and secondary amines with diazo-salts: (1 *a*) Primary aromatic amines yield diazoamido- or disdiazoamido-bodies, depending upon the conditions of experiment. Diazoamido-compounds are formed when equimolecular quantities of diazo-salt and primary amine interact:

$$C_6H_5N_2.Cl + NH_2.C_6H_5 = C_6H_5N = N - NHC_6H_5 + HCl.$$

They are also produced when an alkali nitrite, in the absence of mineral acids, acts upon the salts of primary amines:

$$2C_6H_5NH_2HCl + NO_2K = C_6H_5N = N - NH.C_6H_5 + KCl + HCl + 2H_2O.$$

(1*b*) A disdiazo-compound results if a molecule of aniline be allowed to act in alkaline, alcoholic solution upon two molecules of a diazobenzene salt. It can also be obtained by transposing diazobenzene chloride with diazoamidobenzene (B. **27**, 703):

$$2C_6H_5N_2Cl + C_6H_5NH_2 = \begin{matrix} C_6H_5N = N \\ C_6H_5N = N \end{matrix}{>}N.C_6H_5 + 2HCl$$

$$C_6H_5N_2Cl + C_6H_5N = N - NH.C_6H_5 = \begin{matrix} C_6H_5N = N \\ C_6H_5N = N \end{matrix}{>}N.C_6H_5 + HCl.$$

When a diazobenzene salt solution is allowed to flow into cold, concentrated ammonia, *disdiazobenzeneamide*, $C_6H_5N : N.NH.N : NC_6H_5$ (B. **28**, 171), will be produced.

Course of the Reaction in the Formation (1a) of Diazoamido-derivatives.—It is an interesting fact that the same diazobenzene-p-amidotoluene is formed, *e. g.*, from diazobenzene chloride and p-toluidine, as from diazo-p-toluene chloride and aniline, although different compounds, might well have been expected:

$$C_6H_5N_2Cl + NH_2[4]C_6H_4[1]CH_3 \longrightarrow \text{I. } C_6H_5N = N - NH[4]C_6H_4[1]CH_3$$
$$CH_3[1]C_6H_4[4]N_2Cl + NH_2C_6H_5 \longrightarrow \text{II. } CH_3[1]C_6H_4[4]N = N - NH.C_6H_5.$$

This behavior would justify the assumption that the same intermediate product is formed in both instances by the addition of the primary base with simultaneous breaking down of the double nitrogen union:

$$C_6H_5NH - NCl - NH[4]C_6H_4[1]CH_3.$$

The same compound can then result if hydrochloric acid be eliminated, it being immaterial from which bodies the synthesis began (B. **14**, 2447; **21**, 3004). Hence, the decomposition of a diazoamido-body by an haloid acid cannot be used in ascertaining its constitution, because the haloid acid would first form an addition product. For this purpose phenylisocyanide seems better adapted. Thus, diazobenzene-p-amidotoluene forms a urea with this reagent, and this new compound will have either formula I′, corresponding to I, or II′, corresponding to formula II, depending upon the constitution of the diazoamido-body:

$$\text{I}'.\ CO{<}\begin{matrix} NH.C_6H_5 \\ N{<}\begin{matrix}[4]C_6H_4[1]CH_3 \\ N = N.C_6H_5\end{matrix} \end{matrix} \longrightarrow CO{<}\begin{matrix} NH.C_6H_5 \\ NH[4]C_6H_4[1]CH_3 \end{matrix} + C_6H_5OH + N_2$$

$$\text{II}'.\ CO{<}\begin{matrix} NH.C_6H_5 \\ N{<}\begin{matrix}C_6H_5 \\ N = N[4]C_6H_4[1]CH_3\end{matrix} \end{matrix} \longrightarrow CO{<}\begin{matrix} NH.C_6H_5 \\ NH.C_6H_5 \end{matrix} + CH_3[1]C_6H_4[4]OH + N_2$$

On decomposing the urea with dilute sulphuric acid the products will be phenyl-p-tolyl urea, phenol, and nitrogen; whereas, according to formula II′, they should be sym. diphenylurea, p-cresol, and nitrogen. Therefore, diazobenzene-amido-p-toluene is constituted according to formula I. The imide group apparently combines with the more negative radical (H. Goldschmidt, B. **21**, 2578). Granting the diazonium formula for the diazo-salts, it will of course be necessary to alter the preceding explanation somewhat.

The normal diazo-alkali salts (p. 102) also yield diazoamido-derivatives. Consult B. **29**, 289, for the occurring changes. The isodiazo-salts, resulting from rearrangement of the normal salts, are not reactive.

(*1b*) Primary aliphatic amines also yield diazoamido- and disdiazoamido-bodies (B. **22**, 934). (*1c*) Secondary aliphatic amines form mixed fatty-aromatic diazo-amido-derivatives (B. **8**, 148, 843).

2. Diazoamido-compounds are also formed in the action of free nitrous acid upon the alcoholic solutions of free primary amines; the free diazobenzene hydrate or anhydride produced at first (p. 102) is transposed by aniline:

$$C_6H_5N_2.OH + NH_2.C_6H_5 = C_6H_5N = N—NH.C_6H_5 + H_2O.$$

The action of nitrites—*e.g.*, silver nitrite upon free aniline—produces salts of diazo-amido-bodies, $C_6H_5N_2.NAgC_6H_5$ (B. **29**, R. 1158).

3. They can also be obtained by the action of the nitrosoamines upon the primary amido-bodies. Phenylmethylnitrosamine and aniline yield diazoamidobenzene:

$$\genfrac{}{}{0pt}{}{C_6H_5}{CH_3}{>}N.NO + NH_2.C_6H_5 = \genfrac{}{}{0pt}{}{C_6H_5}{CH_3}{>}N.N:N.C_6H_5 + H_2O.$$

Nitrosoacetanilide (p. 98) and aniline also react, the products being diazoamidobenzene and acetic acid. When one molecule of aniline is used with two molecules of nitrosoacetanilide, and these bodies are allowed to react in alkaline solution, an aromatic disdiazoamido-compound is produced:

$$\genfrac{}{}{0pt}{}{C_6H_5}{CH_3.CO}{>}N—NO + NH_2.C_6H_5 = C_6H_5NH—N = NC_6H_5 + CH_3.COOH$$

$$2\ \genfrac{}{}{0pt}{}{C_6H_5}{CH_3.CO}{>}N—NO + NH_2.C_6H_5 = \genfrac{}{}{0pt}{}{C_6H_5N = N}{C_6H_5N = N}{>}NC_6H_5 + 2CH_3.COOH.$$

Diazoamido-compounds from primary, aromatic bases.

Diazo-amido-benzene, *Benzenediazoanilide, Diazobenzeneanilide* (B. **14**, 2443 Anm.), $C_6H_5.N_2.NH.C_6H_5$, melts at 96° and explodes when it is heated to higher temperatures. It is obtained by the action of nitrous acid on the cold alcoholic solution of aniline (Griess, A. **121**, 258); by mixing diazobenzene nitrate with aniline (B. **7**, 1619); and by pouring a slightly alkaline sodium nitrite solution upon aniline hydrochloride (B. **8**, 1074) or sulphate (B. **17**, 641; **19**, 1953; **20**, 1581).

Diazo amidobenzene consists of golden-yellow, shining laminæ or prisms. It is insoluble in water, sparingly soluble in cold, but readily in hot alcohol, ether, and benzene. Its transpositions will be discussed later; the most remarkable one is its rearrangement into isomeric *amido-azobenzene* (p. 115).

Its salts are very unstable, although it forms a double salt $(C_{12}H_{11}N_3.HCl)_2.PtCl_4$, with hydrochloric acid and $PtCl_4$. It crystallizes in reddish needles. When the alco-

holic solution is mixed with silver nitrate, the compound, $C_6H_5.N_2NAg . C_6H_5$, separates in reddish needles.

Sodium in ethereal solution converts it into $C_6H_5NNaN = N . C_6H_5$, which is decomposed by water (B. **27**, 2315).

Benzene diazoacetanilide, $C_6H_5N = N — N(COCH_3)C_6H_5$, melts with decomposition at 130°, and is formed when diazo-amido benzene stands with acetic anhydride in toluene solution (B. **24**, 4156).

The para-variety of the three *diazo-amido toluenes* is alone stable. The ortho- and meta-forms (from ortho- and meta-toluidine) immediately pass into isomeric amido-azo-derivatives.

Diazo-amido-compounds containing two different aromatic residues: Mixed diazo-amido-compounds, like *diazobenzene*-p-*amidobrombenzene*, melting at 91° (B. **20**, 3012), o-, m-, p-*Dinitrodiazoamido-benzene*, melting at 196°, 194°, 228° (B. **27**, 2201; **28**, R. 303), *diazobenzene*-p-*amidotoluene*, can be obtained from the diazo-derivatives of the two components with the free amido-derivatives—*e. g.*, diazobenzene-p-amidotoluene equally well from the diazobenzene salt with p-toluidine, as from p-diazotoluene salt and aniline. The explanation of this peculiar behavior is given on page 107.

Disdiazobenzene Amide, $(C_6H_5N : N)_2NH$ (B. **27**, 899), is extremely decomposable. *Disdiazobenzene Anilide*, $C_6H_5N = N — N(C_6H_5) — N = NC_6H_5$, consists of shining yellow leaflets, which explode at 80–81° in a capillary tube (B. **27**, 703).

Mixed fatty-aromatic Diazoamido compounds.

Diazobenzene-ethylamine, $C_6H_5N = N — NH . C_2H_5$(?), is a yellow oil. *Diazobenzene-dimethylamine*, $C_6H_5N = N — N(CH_3)_2$, is a yellow oil (B. **8**, 148).

Diazobenzene-piperidine, $C_6H_5N = N — NC_5H_{10}$, melts at 43°. The diazopiperidines are of practical value in the preparation of fluorine derivatives (p. 58) which result upon acting with concentrated hydrofluoric acid upon them (A. **235**, 242; **243**, 223).

Disdiazobenzene-methylamine, $(C_6H_5N = N)_2NCH_3$, consists of bright yellow needles, melting at 112°. *Disdiazobenzene-ethylamine* melts at 70° (B. **22**, 934).

The Rearrangements of the Diazoamido-compounds.—(1) The most remarkable property of the diazoamido-compounds containing a replaceable hydrogen atom in the p-position with reference to the NH-group, is their ability to rearrange themselves into isomeric p-amidoazo-derivatives. *In the amidoazo-body the amido-group holds the p-position with reference to the point of union* (p. 115):

$$C_6H_5N = N—NHC_6H_5 \longrightarrow C_6H_5N = N[1]C_6H_4[4]NH_2.$$

This rearrangement completes itself in the course of a few days, when a small quantity of an aniline salt is present. It may be assumed that in the conversion a quantity of aniline, equal to that actually needed for the change, is produced; consequently a comparatively small amount of the aniline salt will be sufficient to rearrange a large quantity of diazo-amido-benzene into amido-azobenzene (Kekulé, Z. f. Ch. (1866), 689; B. **25**, 1376). The rapidity of the conversion is proportional to the strength of the acid, whose aniline salt is employed (B. **29**, 1899). A *strong base*, such as amidoazobenzene, is obtained from a body indifferent to acids—*e. g.*, diazoamidobenzene. *Various intramolecular atom-rearrangements, such as the preceding, in which indifferent compounds are rearranged to strong bases or strong acids are known—e. g., the rearrangement of hydrazobenzene into benzidine, of benzil into benzilic acid*, etc. (I, 54; II, 116, 118).

(2) The imide hydrogen of the diazoamidobenzene can be replaced by acid radicals through the action of acid anhydrides (see benzene diazoacetanilide).

(3) The diazoamido-compounds and phenylisocyanate combine to urea derivatives. Consult p. 108 upon the importance of this reaction.

In the preceding reactions the diazoamido-bodies are not decomposed. This occurs very readily (4) on treating them with concentrated haloid acids; the diazoamido-derivatives, like the diazobenzene salts, then change to haloid benzenes; the side products are salts of the bases previously in combination with the diazo-residue. Therefore, the diazoamido-compounds, *in the presence of acids*, are fully converted by nitrous acid into diazobenzene salts. The deportment of the diazo-amido-bodies toward concentrated hydrofluoric acid with the addition of diazopiperidines, proved itself particularly well adapted for the preparation of fluorbenzenes (A **243**, 220):

$$C_6H_5N = N - NC_5H_{10} + 2HFl = C_6H_5Fl + N_2 + HFl.HNC_5H_{10}.$$

(5) Boiling water converts the diazoamido-compounds into phenols and bases.

(6) The reduction of the diazoamido-bodies has not led to hydrazoamido-derivatives—*e. g.*, $C_6H_5NH - NH.NH.C_6H_5$; a decomposition into phenylhydrazine and aniline has been the usual result.

(7) On boiling the alcoholic solution with sulphurous acid, the diazo-group is replaced by the sulpho-group:

$$C_6H_5.N_2.NH.C_6H_5 + 2SO_2 + 2H_2O = C_6H_5.SO_3H + N_2 + NH_2.C_6H_5.SO_3H_2.$$

11. DIAZO-OXYAMIDO-COMPOUNDS.

These compounds result from the interaction of diazo-bodies with alkyl- and alphyl-hydroxylamines.

Diazo-oxyamido-benzene, $C_6H_5N_2.N(OH)C_6H_5$, melting at 127°, consists of yellow, silky needles. It is formed as well from nitrosobenzene and phenylhydrazine, as from diazobenzene and phenylhydroxylamine. p-*Nitrobenzene-diazoxyamido-methane*, $NO_2C_6H_4N_2N(OH)CH_3$, melts at 228° (B. **29**, 103).

12. DIAZOIMIDO-COMPOUNDS.

The diazoimido-compounds are ethers of *hydronitric acid—hydrazoic acid*. They are produced:

(1) By the action of aqueous ammonia upon diazobenzene perbromides:

$$C_6H_5.N_2.Br_3 + NH_3 = C_6H_5.N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. + 3HBr.$$

(2) By the action of hydroxylamine upon diazobenzene sulphate (B. **25**, 372; **26**, 1271):

$$C_6H_5.N_2.SO_4H + NH_2OH = C_6H_5.N_3 + H_2O + SO_4H_2.$$

(3) By the action of sodium nitrite upon the hydrochloric acid solution of phenylhydrazine, when the nitrosophenylhydrazine first produced sustains decomposition:

$$C_6H_5.N{<}^{NH_2}_{NO} = C_6H_5N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. + H_2O.$$

(4) From phenylhydrazine and diazobenzene sulphate (B. **20**, 1528; **21**, 3415):

$$C_6H_5N:N.NH.NH.C_6H_5 = C_6H_5NH_2 + C_6H_5N_3.$$

(5) Hydrazine and diazobenzene sulphate yield, on the one hand, diazobenzene imide and ammonia, upon the other, aniline and azoimide or hydronitric acid as side products. These reactions are due to the breaking-down of a non-accessible intermediate product, $C_6H_5N = N - NH.NH_2$ (B. **26**, 88, 1271) (compare buzylene derivatives, p. 131):

$$C_6H_5N = N—NH—NH_2 = C_6H_5N_3 + NH_3$$

$$C_6H_5N = N—NH—NHH = C_6H_5NH_2 + N_3H.$$

Diazobenzene Imide, *Phenylhydronitric Ester*, $C_6H_5N_3$, boiling at 59° (12 mm.), is a yellow oil with stupefying odor. It explodes at the ordinary pressure if heated.

o-*Nitrodiazobenzene Imide*, $NO_2C_6H_4N_3$, melts at 52°. m-*Nitrodiazobenzene Imide* melts at 55°. p-*Nitrodiazobenzene Imide* melts at 74°.

Transformation of the Diazobenzene-imido-compounds.—(1) They are decomposed into N_2 and chloranilines when boiled with hydrochloric acid (B. **19**, 313).

(2) They break down, when boiled with sulphuric acid, into nitrogen and amidophenols (B. **27**, 192).

(3) The diazobenzene imide compounds, nitrated in the o- and p-positions, decompose in part when boiled with alcoholic potash into nitrophenols and hydrazoic acid (B. **25**, 3328).

13. AZOXY-COMPOUNDS.

Formation.—(1) By reduction of nitro- and nitroso-compounds with methyl or ethyl alcoholic potash solutions (B. **26**, 269):

$$4C_6H_5NO_2 + 3HCH_2ONa = 2(C_6H_5N)_2O + 3HCO_2Na + 3H_2O.$$

Sodium amalgam and alcohol, zinc dust in alcoholic ammonia, and arsenious acid in alkaline solution (B. **28**, R. 125) reduce nitro-bodies to azoxy-compounds.

(2) By the oxidation of amido- and azo-derivatives (Z. f. Ch. (1866) 309; B. **6**, 557; **18**, 1420), as well as by the spontaneous oxidation of β-phenylhydroxylamine (p. 70) in the air.

Deportment.—1. When reduced by heating with iron filings they yield azo-compounds, with ammonium sulphide hydrazo derivatives, and with acid reducing agents amido-bodies, resulting from the decomposition and rearrangement of the hydrazo-compounds first produced. 2. Their rearrangement into oxy-azo-compounds, on digesting them with concentrated sulphuric acid, is interesting (Wallach and Belli, B. **13**, 525).

Azoxybenzene, ***Azoxybenzide***, $C_6H_5—N\overset{O}{—}N—C_6H_5$, forms long, yellow needles, easily soluble in alcohol and ether, but not in water. It melts at 36°, and decomposes into azobenzene and aniline when distilled.

It is converted into p oxyazobenzene by digestion with concentrated sulphuric acid.

sym.-m-*Dinitroazoxybenzene*, from m-dinitrobenzene (B. **25**, 608), melts at 141°. sym.-m-*Diamidoazobenzene*, Azoxyaniline, melts at 147° (B. **29**, R. 137).

p-*Tetramethyldiamido-azoxybenzene*, from nitrosodimethyl aniline, melts at 243°. *Trinitroazoxybenzenes* are obtained from azoxybenzene (B. **23**, R. 104).

o-*Azoxytoluene* melts at 59°. m-*Azoxytoluene* melts at 38°. p-*Azoxytoluene* melts at 70°.

14. AZO-COMPOUNDS.

Like the diazo-derivatives, these contain a group, consisting of two nitrogen atoms; in the former the N_2-group is combined with only one benzene nucleus and an inorganic residue; here it is attached on either side to benzene nuclei, or to a benzene nucleus and an aliphatic radical:

$C_6H_5 - N = N - C_6H_5$	$C_6H_5 - N = N - CH_3$
Azobenzene	Benzene Azomethane.

In consequence, they are far more stable than the former, and do not react with the elimination of nitrogen.

Classification and Nomenclature.—The true aromatic azo-bodies are distinguished as *symmetrical*, those in which the two residues are the same, and *unsymmetrical*, those in which the two residues are dissimilar. *Mixed azo-bodies* are those in which the azo-group joins an aromatic to an aliphatic radical.

The names of the unsymmetrical azo-bodies are derived from the names of the two bodies in which the azo-group has replaced an atom of hydrogen each, separated by the word azo,—thus: $C_6H_5 - N = N - C_6H_4N(CH_3)_2$, benzene-azo-dimethyl aniline; $C_6H_5 - N = N - CH_3$, benzene azomethane. Should the benzene residues contain substituents, the positions in the one residue are indicated with numbers 1 to 6, and in the second residue by numbers 1′ to 6′, with the understanding that the azo-group occupies the 1,1′-position.

Disazo- and trisazo-compounds, containing two or three azo-groups, are known (B. **15**, 2812).

Formation.—1. By the moderated reduction of nitro-bodies in *alkaline* solution, because in *acid* solution the final reduction products of nitro-bodies, the amido-derivatives, are almost invariably produced. Azoxy-compounds are first formed, but by further reduction they pass into azo-derivatives. The reducing agents are:

(*a*) Zinc-dust in alcoholic potash or soda (B. **21**, 3139), or in ammonia;

(*b*) Sodium amalgam and alcohol;

(*c*) Stannous chloride in sodium hydroxide (B. **18**, 2912).

By more complete reduction hydrazo-bodies are formed, along with the azo-derivatives; these can eventually be decomposed into amido-compounds. Azobenzene is the middle member in the series of reduction products obtained from nitrobenzene, if *β*-phenylhydroxylamine is not taken into consideration:

$$\underset{\text{Nitrobenzene}}{C_6H_5 . NO_2} \longrightarrow \underset{\text{Azoxybenzene}}{\begin{matrix} C_6H_5 . N \\ C_6H_5 . N \end{matrix}\!\!>\!O} \longrightarrow \underset{\text{Azobenzene}}{\begin{matrix} C_6H_5 . N \\ \| \\ C_6H_5 . N \end{matrix}} \longrightarrow \underset{\text{Hydrazobenzene}}{\begin{matrix} C_6H_5 . NH \\ | \\ C_6H_5 . NH \end{matrix}} \longrightarrow \underset{\text{Aniline.}}{C_6H_5 . NH_2}$$

2. By reduction of azoxy-compounds on heating them with iron filings.

3. By the oxidation (*a*) of hydrazo-bodies (p. 116), and (*b*) of primary amido-derivatives in alkaline solution with potassium permanganate (A. **142**, 364) or with potassium ferricyanide.

4. By the action of nitrosobenzene (p. 70) upon aniline.

5. By the rearrangement of certain diazoamido-bodies into amido-azo-derivatives (p. 114).

6. By action of diazo-salts (*a*) upon tertiary anilines, and (*b*) upon m diamines.

The last two methods lead to amido-derivatives of the azo-hydrocarbons, some of which have become very important for the coal-tar color industry.

Mixed azo-derivatives are frequently obtained by combining diazo-salts with suitable fatty bodies—*i. e.*, such as contain easily replaceable hydrogen atoms in union with carbon, or with heterocyclic compounds like pyrrol, pyrazole, etc.

Properties.—The azo-bodies are more intensely colored than the pale-yellow azoxy-derivatives. They do not unite with acids, if they do not contain an additional basic amido-group. They can be directly chlorinated, nitrated, and sulphonated. Reducing agents convert them into hydrazo-compounds (p. 116), or decompose them at the point of double union with the production of amido-compounds. The latter reaction serves to determine the constitution of the amidoazo-derivatives.

Indifferent, Symmetrical Azo-compounds.—Azobenzene, *Azobenzide*, $C_6H_5N = NC_6H_5$, melting at 68° and boiling at 293°, was discovered by Mitscherlich in 1834. It forms orange-red, rhombic crystals, readily soluble in alcohol and ether, but sparingly soluble in water. It is produced by the methods outlined above from nitrobenzene, aniline, and hydrazobenzene. Azoxybenzene yields it on distillation with iron filings (B. **207**, 329). It has also been obtained from potassium aniline by action of air, and from aniline and sodium (B. **10**, 1802). It is converted into benzidine by tin and hydrochloric acid; this is due to a transposition of the hydrazobenzene first formed.

o-*Nitroazobenzene* melts at 127° (B. **19**, 2157; R. 441). p-*Nitroazobenzene* melts at 137°. sym.-m-*Dinitroazobenzene* is an oil (B. **18**, R. 627). p-*Dinitroazobenzene* melts at 206°. *Dinitrobenzene-azobenzene* melts at 117° (B. **21**, R. 400; **22**, R 744).

Azotoluenes.—o-*Azotoluene* melts at 157°. m-*Azotoluene* melts at 55°. p-*Azotoluene* melts at 143° (B. **17**, 463; **18**, 2551). *Azoxylenes* and *azotrimethyl benzenes* are known.

Mixed Azo-compounds.—*Benzene-azomethane*, azophenylmethane, $C_6H_5N = NCH_3$, boiling at about 150°, and *Benzene-azoethane*, $C_6H_5 . N = NCH_2 . CH_3$, boiling at about 180°, are liquids with a peculiar odor. They are obtained by oxidizing the corresponding hydrazines with mercuric oxide. Sulphuric acid transposes benzene-azoethane into the isomeric acetaldehyde-phenylhydrazine, $C_6H_5NH . N : CH . CH_3$ (B. **29**, 794). *Ben-*

zene azo-nitroethane, $C_6H_5N = NCH(NO_2).CH_3$, melting at 137°, formed from diazobenzene nitrate and sodium nitroethane, consists of orange-colored laminæ, and forms salts with two equivalents of alkali (B. 8, 1076; 9, 384).

Other compounds which can be regarded as mixed azo-derivatives are the *benzenediazocarboxylic acids* and their derivatives, the *diazocyanides* (p. 103), *diphenylsulphocarbazone* and *-carbdiazone* (p. 128), the *formazyl* compounds (p. 129), *benzoyl-diazobenzene* (see this), as well as numerous azo bodies resulting from the combination of diazo-salts with suitable heterocyclic derivatives—*e. g.*, pyrrol, pyrazole, etc.

Amidoazo-compounds.—The indifferent azo-derivatives are all orange-yellow to orange-red in color, but they are not dyes. By the introduction of a salt-forming group the resulting bodies, like amido-azo-compounds, oxyazo-compounds, and especially amidoazobenzene sulphonic acids, do become colors applicable in the dyeing of wool and silk. The number of azo-dyes is very great. Some of the simplest will be discussed in the following paragraphs, while the most important representatives of the class, technically speaking, will be considered in other portions of this book, particularly in connection with the naphthalene group. The sulphonic acids of the amidoazo-bodies are of greater importance than the parent substances.

Formation.—(1) From diazoamido-compounds: p-amidoazobenzene is obtained from diazoamidobenzene. In the case of diazoamidobenzene this transposition occurs on standing with alcohol, but more readily by the action of a slight quantity of aniline hydrochloride.

This reaction only occurs readily if in the reacting diazoamido-compound the position in the benzene nucleus adjacent to the amido-group in the para place be unoccupied.

However, compounds, like diazoamido-p-toluene, $CH_3[4]C_6H_4[1]N = N - NH[1']C_6H_4[4']CH_3$, in which the p-position with reference to the imido-group is occupied by CH_3, also suffer this transposition. It occurs on heating diazoamido-p-toluene, dissolved in fused p-toluidine, to 65° with p-toluidine.

The amido-group of the resulting amido-azo-toluene occupies the o-position with reference to the diazo-group. It is *o-amidoazotoluene* or [4] *Methyl-benzene-azo*-[4']-*methyl*-[2']-*amidobenzene*, $CH_3[4]C_6H_4[1]N = N[1']C_6H_3[4']CH_3[2']NH_2$ (B. 17, 77).

(2) By the action of the diazo-compounds (*a*) upon the tertiary aromatic amines, or (*b*) upon m-diamines in neutral or feebly acid solution (B. 10, 389, 654):

$$C_6H_5.N_2.NO_3 + C_6H_5N(CH_3)_2 = C_6H_5.N = N.[1]C_6H_4[4]N(CH_3)_2 + NO_3H$$

$$C_6H_5.N_2.NO_3 + C_6H_4\left\{\begin{matrix}[1]NH_2\\ [3]NH_2\end{matrix}\right. = C_6H_5.N = N.[1]C_6H_3\left\{\begin{matrix}[2]NH_2\\ [4]NH_2\end{matrix}\right. + NO_3H.$$

The first products with primary and secondary monamines, especially in neutral or acetic acid solution (B. 24, 2077), are diazoamido-compounds, which under the previously mentioned conditions are capable of rearranging themselves into amidoazo-derivatives.

The phenols act like the tertiary amines upon diazo-salts with the formation of oxyazo derivatives, which will be discussed later after the amidophenols.

Properties and Deportment.—The amido-azo-compounds are usually crystalline, and generally dissolve readily in alcohol. They are yellow, red, or brown in color. Their salts with acids are the valuable technical amido-azo-dyes. (1) Their decomposition upon reduction and the great importance of this reaction have been previously dwelt upon (p. 113) (B. **21**, 3471). Occasionally, decomposition such as this takes place on heating the bodies with hydrochloric acid (B. **17**, 395). (2) Amido-azo-compounds may be changed to diazo-azo-derivatives with nitrous acid. *Isodihydrophen-tetrazines* may be obtained by reducing the diazo-salts of o-amido-azo-derivatives. (3) *Indulines* (see these) are produced on heating p-amido-azo-compounds with aniline hydrochloride, and *eurhodines* when o-amido-azo-bodies are employed. (4) When the o-amidoazo-compounds are oxidized they become *pseudoazimido*-derivatives. (5) The o-amido-azo-compounds combine with aldehydes. Condensation products result, which are derived from *dihydrophentriazine* (see this).

Many chemists consider the o-amido-azo-compounds to be *quinon-imides*: $C_6H_5NHN = C_6H_4 = NH$ or $C_6H_5NHN—C_6H_4—NH$ (B. **23**, 497); compare o-azophenols.

p-**Amido-azobenzene**, $C_6H_5—N = N[1]C_6H_4[4]NH_2$, consists of yellow leaflets or needles, melting at 123° and boiling undecomposed above 360°, but at 225° under 12 mm. It can be obtained from p-nitro-azobenzene (p. 113), and is made technically by the rearrangement of diazoamidobenzene (p. 109) (B. **19**, 1953; **21**, 1633), which does not need to be isolated for this purpose. Manganese dioxide and sulphuric acid oxidize it to quinone. It breaks down into aniline and p-phenylene-diamine upon reduction (p. 95). Its hydrochloride forms steel-blue needles and, like the oxalate, has been applied as a yellow dye. It is prepared in the coal-tar industry upon a large scale, and serves as the starting-out material for the manufacture of disazo-dyes and *indulines*. Although the salts of amidoazobenzene have not any importance as dyes, yet the sulphonic acids, *acid yellow* or *pure yellow* (p. 138), possess more valuable and desirable dyeing properties. p-*Acetamido-azo-benzene* melts at 143°.

m-*Amidoazobenzene*, $C_6H_5N_2[1]C_6H_4[3]NH_2$, melts at 57°; its *acet*-derivative, melting at 131°, has been obtained from nitrosobenzene and acet-m-phenylene-diamine (B. **28**, R. 982).

Benzene-azo-p-*dimethylaniline*, $C_6H_5N = N[1]C_6H_4[4]N(CH_3)_2$, melts at 116°. *Benzene-azo-diphenylamine*, p-phenylamido- or p-anilido-azobenzene, melts at 82°. o-*Amidoazotoluene*, $CH_3[2]C_6H_4[1]N = N[1']C_6H_3\begin{cases}[3']CH_3\\[4']NH_2\end{cases}$, melting at 100°, is obtained from o-toluidine. m-*Amido-azo-toluene*, $CH_3[3]C_6H_4[1]N = N[1']C_6H_3\begin{cases}[2']CH_3\\[4']NH_2\end{cases}$, melts at 80°. m-*Nitrobenzene-azo*-p-*amidobenzene* melts at 213° (B. **29**, R. 661).

2,4-**Diamido-azo-benzene**, $C_6H_5 . N_2 . C_6H_3(NH_2)_2$, is produced by the action of diazobenzene-nitrate upon meta-phenylenediamine, and consists of yellow needles melting at 117°. Its hydrochloric acid salt

occurs in trade under the name *chrysoïdine*, and dyes orange-red. Reduction changes it to aniline and unsymmetrical triamido-benzene, C_6H_3-$(NH_2)_3$ (p. 97).

Symmetrical p-**Diamido-azo benzene**, $H_2N . C_6H_4 . N_2 . C_6H_4 . NH_2$, has been prepared by reducing nitroacetanilide, $NO_2 . C_6H_4 . NH . C_2H_3O$, with zinc dust and alkali; also, from diazo-phenylenediamine, etc. (B. 18, 1145), and by the reduction of p-dinitro-azobenzene (see above) (B. 18, R. 628). It crystallizes from alcohol in yellow needles, melting at 241°.

Its tetra-alkylic derivatives are the so-called *Azylines*. They are formed when nitric oxide acts upon the tertiary anilines (B. 16, 2768):

$$2C_6H_5 . NR_2 \text{ yield } R_2N . C_6H_4 . N_2 . C_6H_4 . R_2N,$$

and in the action of the diazo-compounds of dimethyl-p-phenylenediamine (p. 95) upon tertiary anilines (B. 18, 1143):

$$(CH_3)_2N . C_6H_4 . N_2Cl + C_6H_5N(CH_3)_2 = (CH_3)_2N . C_6H_4 . N_2 . C_6H_4N(CH_3)_2 + HCl.$$

The azylines are red, basic dyes, which dissolve in hydrochloric acid with a purple-red and in acetic acid with an emerald-green color. By reduction (stannous chloride, tin, and hydrochloric acid) they yield two molecules of dialkylic p-phenylenediamine. They are decomposed when heated to 100° with alkyl iodides (4 molecules); the products in this case are tetra-alkylic para-phenylenediamines.

Triamido-azo-benzene, $C_{12}H_{13}N_5 = H_2N . C_6H_4 . N_2 . C_6H_3 \lt{}^{NH_2}_{NH_2}$, is formed when nitrous acid acts upon metaphenylene-diamine. At first, by transformation of an amido-group, we obtain a diazo-compound, which further reacts on a second molecule of the diamine. It forms salts with one, two, and three equivalents of the acids; of these the diacid are the most stable, while water decomposes the triacid. Its hydrochloric acid salt, mixed with *Tetraamidophenylene-bis-azobenzene*, $C_6H_4[N_2C_6H_3(NH_2)_2]_2$, is commercial *Phenylene Brown* (Manchester-brown, Bismarck-brown), which is applied in dyeing cotton and coloring leather.

15. HYDRAZINE COMPOUNDS.

The simplest aromatic hydrazine derivatives are: *Phenylhydrazine*, $C_6H_5 . NH . NH_2$; unsym.-*Diphenylhydrazine*, $(C_6H_5)_2N . NH_2$, and sym.-*Diphenylhydrazine*, $C_6H_5NH . NH . C_6H_5$, or *hydrazobenzene*.

Phenylhydrazine and unsym.-diphenylhydrazine both contain an NH_2-group. They show similar reactions in many respects, whereas the symmetrical diphenylhydrazine deports itself rather peculiarly. In the following paragraphs sym.-diphenylhydrazine and its homologues, the *hydrazo-compounds*, the hydrazine derivatives longest known, will be placed at the head of the aromatic hydrazines. The hydrazo-compounds arrange themselves with the previously discussed azo-bodies, with which they possess many intimate connections. Then will follow the monophenyl- and the unsym.-diphenylhydrazine group.

Hydrazo-compounds.—Symmetrical diphenylhydrazine was discovered in 1863 by A. W. Hofmann upon reducing azobenzene with care, and inasmuch as it differed from the last compound in containing two hydrogen atoms more, it was called *hydrazobenzene*, a name which has adhered to symmetrical diphenylhydrazine.

Formation.—Azobenzene and allied compounds yield hydrazobenzene upon reducing them with alcoholic ammonium sulphide, with zinc dust, and with potassium or sodium amalgam. It is not necessary to isolate the azo-body; the proper nitro- and azoxy-derivatives can be treated with zinc dust and sodium hydroxide. Nitro-compounds can also be converted in alkaline solution into hydrazo-derivatives by electrolytic reduction (Ch. Ztg. 17, 129, 209).

***Hydrazo-benzene,** sym.-*Diphenylhydrazine*, $C_6H_5 . NH . NH . C_6H_5$, melting at 131°, decomposes at higher temperatures into azo-benzene and aniline. It is readily soluble in alcohol and ether, and crystallizes in colorless plates or leaflets, insoluble in water. It has an odor resembling that of camphor. When its alcoholic solution is exposed to the air, it oxidizes to azo-benzene.

It is an indifferent body, and does not form salts with acids, but concentrated mineral acids occasion in it an interesting transposition. See below, *benzidine* and *semidine* rearrangement.

Powerful reducing agents decompose hydrazobenzene into two molecules of aniline.

Hydrazobenzene yields urea-derivatives with phenylisocyanate (B. 23, 490) and with phenyl mustard oil (B. 25, 3115); with benzaldehyde it forms *diphenylhydrazibenzylene* or *benzhydrazoln*, $C_6H_5CH<\begin{matrix}N . C_6H_5\\ N . C_6H_5\end{matrix}$, melting at 55° (B. 19, 2239).

Monacetyl-hydrazobenzene melts at 159°. *Diacetyl-hydrazobenzene* melts at 105° (B. 17, 379; A. 207, 327).

o-, m-, and p-*Methyl-hydrazobenzene* or sym. o-, m-, and p-*Tolylphenylhydrazine* melt at 101°, 60°, and 86°.

sym.-**Hydrazotoluenes**, $CH_3 . C_6H_4 . NH . NH . C_6H_4 . CH_3$.

The *ortho*-compound melts at 165°; the *meta* is liquid (A. 207, 116), and the *para* melts at 124° (B. 9, 829).

Hydrazoxylenes (B. 21, 3141).

sym.-*Dihalogen hydrazobenzenes* have been obtained from the corresponding azo-bodies.

p-**Diamidohydrazobenzene**, *diphenine*, $NH_2[4]C_6H_4[1]NH . NH[1']C_6H_4[4']-NH_2$, melting at 145°, results from the action of ammonium sulphide upon para-dinitroazo-benzene (B. 18, 1136).

Unsymmetrical *nitrohydrazobenzenes* have been obtained from chlordinitro- and chlortrinitrobenzene by the action of phenylhydrazine (A. 190, 132; 253, 2; J. p. Ch. [2] 37, 345; 44, 67). Compare further asymmetrical polynitrodiphenylamines (p. 93).

Tetraphenylhydrazine, $(C_6H_5)_2N — N(C_6H_5)_2$, melting at 147°, results from the action of iodine upon diphenylamine sodium, $(C_6H_5)_2NNa$ (B. 29, R. 87).

THE BENZIDINE AND SEMIDINE REARRANGEMENT OR TRANSPOSITION OF THE HYDRAZO-COMPOUNDS.

Hydrazobenzene sustains a very remarkable rearrangement into an isomeric compound when it is treated with acids. When azobenzene is reduced in acid solution, the hydrazobenzene which is produced does not form salts, but even in the cold is changed by mere contact with acids into a diamine, a diacid base: *benzidine* (see this) or p-*diamidodiphenyl*. Benzidine, a starting-out substance for the preparation of substantive cotton dyes, is prepared technically in the wet way. **Diphenyline* (see

this), o,p-*diamido-diphenyl* (B. **17**, 1181), occurs in small quantities, together with benzidine:

$$\begin{array}{ccccc} C_6H_4[4]NH_2 & & C_6H_5NH & & C_6H_4[4]NH_2 \\ | & \longleftarrow & | & \longrightarrow & | \\ C_6H_4[4]NH_2 & & C_6H_5NH & & C_6H_4[2]NH_2 \\ \text{Benzidine} & & \text{Hydrazobenzene} & & \text{Diphenyline.} \end{array}$$

The chief or principal rearrangement, in which the two amido-groups arrange themselves in the para-position with reference to the point of union of the two benzene nuclei, is known as the *benzidine rearrangement* of the hydrazo-compounds.

Mineral acids convert sym.-o- and m-ditolyl hydrazine or o- and m-hydrazotoluene and other hydrazo-compounds, in which the p-hydrogen atoms referred to the imido-groups in both aromatic residues are free, into the corresponding p-*diamido ditolyls* or *tolidines*.

If, however, p-hydrazotoluene be treated with aqueous mineral acids, it changes in part to p-azotoluene and p-toluidine, and partly to o-*amidoditolylamine* (B. **27**, 2700). The latter body is principally formed by the action of stannous chloride and hydrochloric acid upon hydrazotoluene:

$$\underset{\text{p-Hydrazotoluene}}{CH_3\frac{H\ H}{H\ H}HN-NH\frac{H\ H}{H\ H}CH_3} \longrightarrow \underset{\text{o-Amido-[4,3']-ditolylamine.}}{CH_3\frac{H\ H}{H\ H}NH\frac{H\ CH_3}{NH_2\ H}H.}$$

Hydrazo benzene itself, when acted upon in benzene with hydrochloric acid gas, yields small amounts of o *amidodiphenylamine* (Ch. Ztg. **18**, 1095):

$$H\frac{H\ H}{H\ H}NH-NH\frac{H\ H}{H\ H}H \longrightarrow H\frac{H\ H}{H\ H}NH\frac{H\ H}{NH_2H}H.$$

This is the *semidine rearrangement*; it is so called because only the one NH-group is converted into an NH_2-group, and not both NH-groups, as in the *benzidine* rearrangement. In simple p-substituted hydrazobenzenes the amido-group can enter the o- or p-position with reference to the imido-group. Hence it is necessary to distinguish between an o- and p-*semidine* transposition.

Acetamidohydrazobenzene, melting at 146°, is changed by stannous chloride and hydrochloric acid into *monacet*-p-*diamidodiphenylamine* (B. **26**, 704):

$$C_2H_3ONH\frac{H\ H}{H\ H}NH-NH\frac{H\ H}{H\ H}H \longrightarrow C_2H_3ONH\frac{H\ H}{H\ H}NH\frac{H\ H}{H\ H}NH_2.$$

Attention may here be directed to such transpositions in which anilines substituted at the nitrogen are converted, by the migration of the substituents, into anilines substituted in the nucleus. Usually, in these changes, compounds with feebly pronounced or neutral character yield more basic bodies. They are:

(1) The rearrangement of the phenylnitrosamines into p-nitroso-anilines (p. 97); (2) that of the phenylnitramines (diazobenzene acids, p. 98) into p-nitranilines; (3) the β-phenylhydroxylamines (p. 70) into p-amidophenols; (4) the phenylhydrazines into p-phenylene-diamines (p. 120); (5) the chlorylanilines into p-chloranilines (see p-chloraniline, p. 92, and μ-methyltolimidazole; (6) the diazoamido- into p-amidoazo-bodies (p. 110); (7) the hydrazobenzenes into benzidines and amidodiphenylamines:

$$\begin{array}{llll} (1)\ C_6H_5N(CH_3)NO & (2)\ C_6H_5NH.NO_2 & (3)\ C_6H_5NH(OH) & (4)\ C_6H_5NH(NH_2) \\ \quad\downarrow & \quad\downarrow & \quad\downarrow & \quad\downarrow \\ \quad NO.C_6H_4.NH(CH_3) & \quad NO_2.C_6H_4NH_2 & \quad (OH)C_6H_4.NH_2 & \quad NH_2.C_6H_4.NH_2 \end{array}$$

$$\begin{array}{llll} (5)\ C_6H_5NHCl & (6)\ C_6H_5NH(N_2C_6H_5) & \multicolumn{2}{l}{(7)\ C_6H_5NH.NH.C_6H_5} \\ \quad\downarrow & \quad\downarrow & \quad\downarrow & \quad\downarrow \\ \quad Cl.C_6H_4.NH_2 & \quad (C_6H_5.N_2).C_6H_4NH_2 & C_6H_5.NH.C_6H_4NH_2 & NH_2.C_6H_4.C_6H_4NH_2 \end{array}$$

Those instances in which carbon groups wander from nitrogen to the nucleus—*e. g.*, the rearrangement of the phenyl alkylamines into homologous anilines (p. 78), etc.—might also be included here. Compare also the transpositions of phenylsulphuric acid and phenylcarbonic acid into phenolsulphonic acid and salicylic acid (p. 147).

Phenylhydrazine Group.—Phenylhydrazine and unsym.-diphenylhydrazine are formed in the reduction of diazobenzene salts and diphenylnitrosamine, as well as from the reaction products produced when nitrous acid acts upon primary and secondary anilines:

$$\begin{array}{lll} C_6H_5NH_2HCl \longrightarrow & C_6H_5N:N.Cl \longrightarrow & C_6H_5NHNH_2HCl \\ (C_6H_5)_2NH \longrightarrow & (C_6H_5)_2N.NO \longrightarrow & (C_6H_5)_2N.NH_2. \end{array}$$

Formation.—1. *By the reduction of diazo-salts:* (*a*) By the action of acid alkaline sulphites upon the diazo-derivatives. On allowing neutral potassium sulphite to act upon the yellow-colored potassium salt of diazobenzene-sulphonic acid, when colorless potassium benzene hydrazine-sulphonate will be formed immediately:

$$C_6H_5—N=N—SO_3K + SO_3HK + H_2O = C_6H_5NH.NHSO_3K + SO_4KH.$$

When the sulphonate is heated with hydrochloric acid, phenylhydrazine hydrochloride is produced, together with primary potassium sulphate:

$$C_6H_5.N_2.H_2.SO_3K + HCl + H_2O = C_6H_5.N_2H_3.HCl + SO_4KH.$$

The *sulphazides*—*e. g.*, $C_6H_5.NH.NH.SO_2.C_6H_5$, *phenyl-benzene sulphazide*—are prepared by the action of free sulphurous acid upon the acid solution of diazobenzene salts.

p-Nitrodiazobenzene nitrate and two molecules of potassium sulphite yield potassium p-nitrophenylhydrazine disulphonate, $C_6H_4(NO_2)N(SO_3K)NH(SO_3K)$, which hydrochloric acid decomposes quantitatively into p-nitrophenylhydrazine.

In the same manner dipotassium sulphite changes potassium benzene diazosulphonate into potassium phenylhydrazine disulphonate, $C_6H_5N(SO_3K)NH(SO_3K)$, which can be more easily obtained from nitrosoacetanilide and dipotassium sulphite (p. 98). It is resolved by hydrochloric acid into phenylhydrazine and sulphuric acid, and decomposed by alkali into potassium benzene diazosulphonate (B. **30**, 374).

(*b*) Potassium diazobenzene sulphonate can be reduced with acetic acid and zinc dust.

(*c*) By the action of stannous chloride and hydrochloric acid upon the diazo-chlorides (B. **16**, 2976; **17**, 572):

$$C_6H_5.N_2Cl + 2SnCl_2 + 4HCl = C_6H_5.N_2H_3.HCl + 2SnCl_4.$$

Diazobenzene alkali salts (p. 102), when reduced with sodium amalgam furnish a good yield of phenylhydrazine (B. **30**, 339).

2. By the reduction of diazo-amido-compounds in alcoholic solution with zinc dust and acetic acid, when they decompose into anilines and hydrazines:

$$\underset{\text{Diazo-amido-benzene}}{C_6H_5.N_2.NH.C_6H_5} + 2H_2 = \underset{\text{Phenylhydrazine}}{C_6H_5.N_2H_3} + \underset{\text{Aniline.}}{NH_2.C_6H_5}$$

3. By the reduction of the nitroso-amines (pp. 97 and 120) with zinc dust and acetic

acid, unsym.-alkylphenyl- or diphenyl-hydrazines are then formed, and the aliphatic hydrazines are obtained in a similar manner (1, 171):

$$\genfrac{}{}{0pt}{}{C_6H_5}{C_6H_5}{>}N.NO + 2H_2 = \genfrac{}{}{0pt}{}{C_6H_5}{C_6H_5}{>}N.NH_2 + H_2O$$

Diphenyl Nitrosamine a-Diphenyl Hydrazine.

Historical.—A. Strecker and Römer, in 1871, obtained potassium phenylhydrazine sulphonate by the interaction of diazobenzene nitrate and acid potassium sulphite, and when the same reagent was allowed to act upon the diazide of sulphanilic acid (p. 137) they got a soluble potassium salt, which, boiled with hydrochloric acid, yielded crystalline phenylhydrazine-p-sulphonic acid, $C_6H_4\left\{\begin{array}{l}[1]NH.NH_2\\ [4]SO_3H\end{array}\right.$, the first primary aromatic hydrazine compound, which must be viewed as a cyclic ammonium salt: $C_6H_4\left\{\begin{array}{l}[1]NH-NH_3\\ [4]SO_3-\!\!\!-\!\!\!|\end{array}\right.$. Emil Fischer, in 1875, demonstrated that potassium phenylhydrazine sulphonate was converted, on boiling with hydrochloric acid, into phenylhydrazine hydrochloride, from which sodium hydroxide liberated phenylhydrazine, an exceedingly reactive substance (B. 8, 589).

Properties.—The aromatic hydrazines are monacid bases, dissolving with difficulty in water, but easily in alcohol and in ether. At the ordinary pressure they boil with slight decomposition and without decomposition under diminished pressure. In the air they oxidize very readily, taking on a brown color. They reduce Fehling's solution.

Phenylhydrazine, $C_6H_5NH - NH_2$, forms plate-like crystals melting at 23°. It boils under 760 mm. at 241–242° with slight decomposition, and under 12 mm. pressure at 120° without decomposition. Its specific gravity at 21° equals 1.091. It is made, as already described under general methods of formation, by the reduction of diazobenzene chloride. Its transpositions are given below. It has, as a generator of *antipyrine,* met with wide application. It serves as an important reagent for the detection of aldehydes and ketones. The latter observation has become of particular importance in the development of the chemistry of the carbohydrates.

Its *hydrochloride,* $C_6H_5NH.NH_2.HCl$, consists of brilliant, white leaflets, dissolving with difficulty in concentrated hydrochloric acid. When it is heated to 200° with hydrochloric acid it yields p-phenylenediamine. For its salts with carboxylic acids consult B. 27, 1521.

Metallic sodium dissolves in phenylhydrazine, forming the sodium derivative, $C_6H_5.NNa.NH_2$. This is a yellowish red, amorphous mass.

Alkyls and acid residues can replace the sodium, thus producing a-phenylhydrazine derivatives (p. 127) (B. 19, 2448; 22, R. 604). *Potassium phenylhydrazine* (B. 20, 47).

Substituted Phenylhydrazines (A. 248, 94; B. 22, 2801, 2809).—p-*Chlorphenylhydrazine* melts at 83°. **p-Bromphenylhydrazine** melts at 106°. p-*Iodphenylhydrazine* melts at 103°. **o-Nitrophenylhydrazine** forms brilliant red needles, melting at 90° (B. 27, 2549).

o-*Nitro-s-formylphenylhydrazide* melts at 177° (B. 22, 2804). For the formation of hetero-rings from these nitro-bodies, see p. 122. p-*Nitrophenylhydrazine* melts at 157° (B. 29, 1831).

Homologous Phenylhydrazines.—*o*-**Tolyl-hydrazine** melts at 59°. *m*-**Tolylhydrazine** is liquid. *p*-**Tolyl-hydrazine** melts at 61°. **Pseudocumyl-hydrazine** (A. 212, 338; B. 18, 91, 3175; 22, 834).

Unsymmetrical diphenylhydrazine, $(C_6H_5)_2N.NH_2$, melting at 34° and boiling at

220° (50 mm.), is made by reducing diphenyl nitrosamine (p. 98). It forms sparingly soluble diphenylhydrazones with glucoses. Ferric chloride oxidizes it to tetraphenyltetrazone (p. 131).

Behavior of the Phenylhydrazines.—(1) While the phenylhydrazines are pretty stable toward reducing agents, they may be readily reconverted into diazo-compounds by moderated oxidation; this is effected by the action of mercuric oxide upon their sulphates or sulphonates.

When boiled with copper sulphate or ferric chloride, the phenylhydrazines throw off nitrogen and become benzenes—this reaction will also serve for the replacement of the diazo-group by hydrogen and by the halogens if the free phenylhydrazine be replaced by chlorine, bromine, or iodine (B. **18**, 90, 786; **25**, 1074). The liberated nitrogen also answers for the quantitative estimation of the hydrazines.

The phenylhydrazines also reduce Fehling's solution (B. **26**, R. 234). Consult B. **28**, R. 996; **29**, R. 977, for additional reduction reactions with phenylhydrazine.

(2) Sodium liberates hydrogen, and α-sodium phenylhydrazines result.

(3) Nitrous acid converts the phenylhydrazines into nitrosohydrazines (p. 131).

(4) The alkylogens replace imido- and amido-hydrogen in the phenylhydrazines, finally forming phenylhydrazonium compounds.

(5) The aldehydes and ketones combine with the phenylhydrazines, usually with the immediate separation of water and formation of *phenylhydrazones*. This reaction, like the oxime formation, is characteristic of the aldehydes and ketones.

(6) Acid radicals can also be readily introduced into the phenylhydrazines.

(7) When the phenylhydrazines are heated to 200° with fuming hydrochloric acid, they are transposed into paraphenylenediamines (see p. 118, and B. **28**, 1538)

Phenylalkyl Hydrazines.—The α-derivatives are termed *symmetrical*, the β-compounds *unsymmetrical* alkylphenylhydrazines. *Formation*: (1) Both isomerides are produced by the action of alkyl bromides upon phenylhydrazine (A. **199**, 325; B. **17**, 2844). (2) The β-class is also obtained by the reduction of the corresponding mixed azo-bodies (p. 112). (3) The α-derivatives are obtained by the action of ethyl bromide upon sodium phenylhydrazine (B. **19**, 2450, 22, R. 664; (4) by reduction of the corresponding nitrosamines (p. 97) with zinc dust; (5) by treating β-acetphenylhydrazine, $C_6H_5NH.NH.CO.CH_3$, with halogen compounds, and saponifying with boiling, dilute acids (B. **26**, 946).

a-Methyl-phenylhydrazine, $C_6H_5.N(CH)_3.NH_2$, melting at 131°(35 mm.), rearranges itself to methyl-p-phenylenediamine.

a-Ethyl-phenyl hydrazine, $C_6H_5.NH.NH(C_2H_5)$, boils at 231°. Both compounds are oxidized to *tetrazones* (p 131).

The α-ethyl compound unites with ethyl bromide to form $C_6H_5.N(C_2H_5)_2Br.NH_2$, which by reduction yields diethyl-aniline.

a-Ethylene Phenylhydrazine, $C_6H_5N<\begin{smallmatrix}NH_2 & NH_2\\ CH_2-CH_2\end{smallmatrix}>N.C_6H_5$, melts at 90° (B. **21**, 3203).

β-Methyl-phenyl hydrazine and *β-Ethyl-phenyl hydrazine* are colorless oils, oxidizing on exposure to air to benzene-azo-methane and -ethane (p. 113), from which they can be obtained by reduction. The β-body can also be produced from *antipyrine* by boiling it with alcoholic potash (B. **25**, 771).

β-Allyl-phenyl hydrazine boils at 177° (110 mm.) (B. **22**, 2233).

The *di-* and *tri-alkylic phenylhydrazines* are formed by letting alkyl iodides act upon the sodium derivative of *α-methyl-phenyl-formyl hydrazine*, $C_6H_5N(CH_3)NNa.CHO$, and then splitting off the formyl group with fuming hydrochloric acid.

Dialkylic phenylhydrazines, by the action of alkyl iodides, are converted into quaternary *azonium* derivatives—*e. g.*, $C_6H_5N(CH_3)_2I.NH.CH_3$—together with trialkyl phenylhydrazines. *αβ-Dimethyl-phenyl hydrazine*, $C_6H_5N(CH_3)NH.CH_3$, boils at 93° (7 mm.); *phenyl-trimethyl hydrazine* boils at 93° (8 mm.) (B. **27**, 696). unsym.-o-*Amido-phenyl-methyl hydrazine*, $NH_2[2]C_6H_4[1]N(CH_3)NH_2$, is an oil which rapidly changes to a resin. It is produced upon reducing o-nitronitrosomethylaniline with alcoholic ammonium sulphide.

Hetero-ring Formations from o-substitution derivatives of phenylhydrazine. Azimidol results on boiling o-nitrophenylhydrazine with caustic alkali. *α-Phentriazine* is produced by reducing the formyl derivative of o-nitrophenylhydrazine with sodium amalgam and acetic acid. unsym.-o-Amido-phenyl-methyl hydrazine is converted by nitrous acid into *phen-methyldihydrotetrazine* :

$$C_6H_4\begin{cases}[1]NH.NH_2\\ [2]NO_2\end{cases} \xrightarrow{KOH} C_6H_4\begin{cases}[1]N = N\\ [2]N(OH)\end{cases} \quad \text{Azimidol}$$

$$C_6H_4\begin{cases}[1]NH.NH.CHO\\ [2]NO_2\end{cases} \xrightarrow{H} C_6H_4\begin{cases}[1]N = N\\ \quad\quad |\\ [2]N = CH\end{cases} \quad \alpha\text{-Phentriazine}$$

$$C_6H_4\begin{cases}[1]N(CH_3)NH_2\\ [2]NH_2\end{cases} \xrightarrow{NOOH} C_6H_4\begin{cases}[1]N(CH_3).N\\ \quad\quad\quad\quad \|\\ [2]NH - N\end{cases} \quad \text{Phenmethyl-dihydrotetrazine.}$$

Phenylhydrazones.—Just as the aldehydes and ketones form oximes with hydroxylamine, so they combine to *phenylhydrazones* with phenylhydrazine. The compounds derived from the aldehydes are termed *aldehydrazones* (A. **247**, 194 Anm.), and those from the ketones are the *ketohydrazones*, while the dihydrazones of the *α*-dicarbonyl-derivatives are the *osazones* (B. **21**, 984):

$$R'.CHO + NH_2NHC_6H_5 = R'.CH = N.NH.C_6H_5 + H_2O$$
$$(R')_2CO + NH_2.NHC_6H_5 = (R')_2C = N.NH.C_6H_5 + H_2O.$$

The osazone formation has become very important for the chemistry of the sugars (see 1, 546).

The phenylhydrazone formation is usually supposed to consist first in the production of an addition product, corresponding in its constitution to aldehyde ammonia. In a few instances—*e.g.*, with oxaloacetic ester and dioxosuccinic ester—it has been possible to isolate the addition products, which split off water with ease and pass into phenylhydrazones:

$$\begin{matrix}CO_2.C_2H_5.CO\\ |\\ CO_2.C_2H_5.CH_2\end{matrix} + NH_2.NH.C_6H_5 = \begin{matrix}CO_2.C_2H_5.C{<}^{NH.NH.C_6H_5}_{OH}\\ |\\ CO_2.C_2H_5\ CH_2\end{matrix}$$

$$\begin{matrix}CO_2.C_2H_5.CO\\ |\\ CO_2.C_2H_5.CO\end{matrix} + 2NH_2.NH.C_6H_5 = \begin{matrix}CO_2.C_2H_5.C{<}^{NH.NH.C_6H_5}_{OH}\\ |\\ CO_2.C_2H_5C{<}^{NH.NH.C_6H_5}_{OH}\end{matrix}$$

That dioxosuccinic ester yields an addition product argues for the aldehyde-ammonia constitution, and against the view possible with oxaloacetic ester, that it is an ammonium salt corresponding to the formula $CO_2.C_2H_5.CO.CH(NH_3.NHC_6H_5).CO_2C_2H_5$ (A. **295**, 339).

As the phenylhydrazones are characteristic for bodies containing the aldehyde and ketone groups, it was but natural that they should have been frequently mentioned in connection with the aliphatic derivatives, and will also be again met with later in con-

nection with the aromatic compounds in which aldehyde and ketone groups are present. It seems, however, advisable to refer briefly to the aliphatic phenylhydrazone derivatives. The following have received mention in the first volume of this work: Phenylhydrazones of the simple aldehydes; of the simple ketones; of the diketones; of glyoxylic acid; of pyroracemic acid; of acetoacetic ester; of lævulinic acid; of mesoxal-aldehyde; of acetone oxalic ester; of mesoxalic acid; of oxalacetic ester; of acetone dicarboxylic ester; of acetone diacetic acid; of tetroses; of oxalyldiacetone; of dioxosuccinic acid; of oxalosuccinic ester; of arabinose; of rhamnose; of the glucoses; of milk sugar; of maltose and isomaltose.

Formation of the Phenylhydrazones.—(1) By the action of phenylhydrazine and unsym.-alkylphenyl or unsym.-diphenyl-hydrazine upon aldehydes and ketones (see above). (2) By the addition of phenylhydrazine to trebly linked carbon atoms; the phenylhydrazone of oxalo-acetic ester is also produced by the addition of phenylhydrazine to acetylene dicarboxylic ester:

$$\begin{array}{l} CO_2.C_2H_5.C \\ \quad\ \ ||| \\ CO_2.C_2H_5.C \end{array} + NH_2NHC_6H_5 = \begin{array}{l} CO_2.C_2H_5.C = N.NH.C_6H_5 \\ \qquad\qquad | \\ CO_2.C_2H_5.CH_2 \end{array}$$

(3) By the interaction of diazobenzene salts and many aliphatic bodies, containing hydrogen atoms readily replaceable by alkali metals—*e.g.*, malonic ester and acetoacetic ester in alkaline solution (potassium diazobenzene, p. 102):

$$(CO_2C_2H_5)_2CH_2 + C_6H_5{-}N_2OH = (CO_2C_2H_5)_2C = N{-}NH.C_6H_5 + H_2O$$

Phenylhydrazone-mesoxaloester

$$\begin{array}{l} CO_2C_2H_5CH_2 \\ \quad | \\ CH_3.CO \end{array} + C_6H_5{-}N_2OH = \begin{array}{l} CO_2C_2H_5C = N{-}NHC_6H_5 \\ \quad | \\ CH_3.CO \end{array} + H_2O$$

Phenylhydrazone-acetoglyoxylic Ester.

The body obtained from diazobenzene and malonic ester is identical with that derived from mesoxalic ester and phenylhydrazine. The idea that these bodies are hydrazones has been proved, among other ways, in the following manner:

(1) Dilute caustic alkali saponifies the phenylhydrazone of acetoglyoxylic ester, and breaks down the acid into carbon dioxide and pyroracemic aldehyde-hydrazone. (2) The latter compound, acted upon with chloracetic ester and sodium ethylate, yields an ester from which anilidoacetic acid is obtained by reduction. This could only be possible if the chloracetic acid residue was joined to the same N-atom, with which the phenyl group had been attached (A. 247, 190):

$$\begin{array}{l} CO_2.C_2H_5.C = N.NHC_6H_5 \\ \quad\ | \\ CH_3.CO \end{array} \longrightarrow CH_3.CO.CH = N{-}NHC_6H_5$$

$$\swarrow$$

$$CH_3.CO.CH = N{-}N\!<\!\begin{array}{l} C_6H_5 \\ CH_2.CO_2.C_2H_5 \end{array} \longrightarrow CO_2.HCH_2NH.C_6H_5$$

The tendency to phenylhydrazone formation is so great that diazobenzene chloride expels carbon dioxide from alkylacetoacetic esters and the acetyl group from alkylic acetoacetic esters, with the production of the phenylhydrazone of an α-diketone and phenylhydrazones of α-ketone carboxylic esters respectively:

$$\begin{array}{l} CH_3.CH.CO_2H \\ \quad\ | \\ CH_3.CO \end{array} + C_6H_5N_2Cl = \begin{array}{l} CH_3.C = N{-}NH.C_6H_5 \\ \quad\ | \\ CH_3.CO \end{array} + CO_2 + HCl$$

Diacetophenylhydrazone (1, 328).

$$\begin{array}{l} CH_3.CH.CO_2.C_2H_5 \\ \quad\ | \\ CH_3.CO \end{array} + C_6H_5N_2Cl + H_2O = \begin{array}{l} CH_3.C.CO_2C_2H_5 \\ \quad\ \| \\ N{-}NHC_6H_5 \end{array} + CH_3.CO_2H + HCl$$

Phenylhydrazone-pyroracemic Ester.

Nitrous acid acts similarly with formation of oximes (vol. 1). (3) Phenylhydrazine converts the monoximes of α-aldehyde ketones and α-diketones into *hydrazoximes*: thus, methylglyoxaloxime yields *methylglyoxalphenylhydrazoxime*, $CH_3 . C = (N - NH\text{-}C_6H_5)CH = NOH$, melting at 134° (A. **262**, 278).

Transpositions of the Phenylhydrazones.—The phenylhydrazones are resolved into their original components on digesting them with dilute mineral acids. By carefully moderated reduction many phenylhydrazones have been converted into phenylhydrazides (see phenylhydrazido-acetic acid, p. 126; B. **28**, 1223); consult B. **30**, 736, upon the oxidation of phenylhydrazones.

Very few classes of organic compounds are capable of entering into the formation of heterocyclic bodies to the extent manifested by the hydrazine derivatives, whose intramolecular condensation reactions are, therefore, of the utmost importance in the development of the chemistry of ring-systems containing nitrogen. Some of the most important condensations have been met in connection with the phenylhydrazones of the fatty compounds, and will be again given in condensed form, while others will receive mention at the conclusion of the acid hydrazides.

(1) *Indols* result upon heating the phenylhydrazones of aldehydes, ketones, and ketonic acids with zinc chloride, stannous chloride, or mineral acids.

(2) *Osotetrazones* are produced when the osazones or α-diphenylhydrazones of α-dialdehydes, α-aldehyde-ketones, and α-diketones are oxidized.

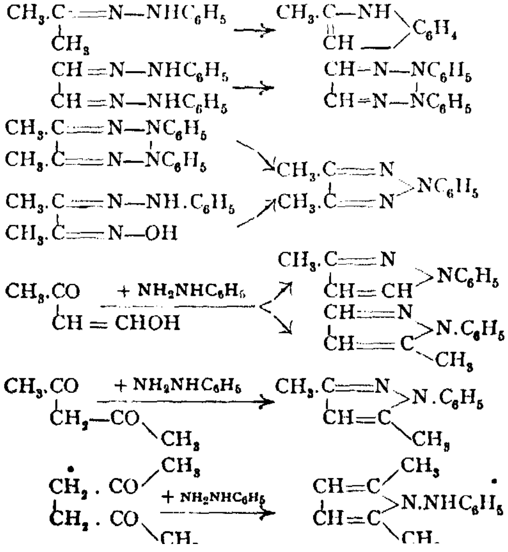
(3) Boiling acids change the α-osazones and osotetrazones to *osotriazoles*.

(4) Dehydrating agents convert α hydrazoximes into *osotriazoles*.

(5) *Pyrazoles* result from the phenylhydrazones of the 1,3-oxymethylene ketones and β-diketones by the exit of water; they are ring-shaped, nitrogen derivatives of the 1,3-olefine ketones.

(6) The phenylhydrazones of 1,4-diketones rearrange themselves into n-*anilidopyrrols*. In preparing ring-shaped condensation products of the hydrazones the latter have frequently not been isolated, but simply worked over.

The following scheme represents the hetero-ring-formations possible with the phenylhydrazones:



α-Methyl Indol, or Methyl Ketol

Glyoxalosotetrazone

Diaceto-osotriazone, or n-Phenyldimethyl-osotriazole

1-Phenyl-3-methyl Pyrazole

1-Phenyl-5-methyl Pyrazole

1-Phenyl-3,5-dimethyl Pyrazole

n-Anilido-α-dimethyl Pyrrol.

PHENYLHYDRAZINE DERIVATIVES OF INORGANIC ACIDS.

Thionyl Phenylhydrazone, $C_6H_5NH.N = SO$, melting at 105°, consists of sulphur-yellow colored prisms. It is obtained, like the *thionyl alkylamines* (1, p. 170) and *thionyl anilines* (p. 80), by the interaction of thionyl chloride and phenylhydrazine. All phenylhydrazines having a free amido-group yield thionyl phenylhydrazones when acted upon with thionyl chloride (B. **27**, 2549). Thionyl phenylhydrazone is more easily produced when thionyl aniline acts upon phenylhydrazine. Further, it results upon gently digesting *phenylhydrazine sulphinic acid*, $C_6H_5NH.NH.SOOH$, obtained from sulphur dioxide and phenylhydrazine (B. **23**, 474). Thionyl chloride, acetyl chloride, and other acid chlorides rearrange thionyl phenylhydrazine into *diazobenzene chloride*, in that it reacts as if it were *diazobenzene sulphoxide* (p. 100), $C_6H_5N = N.S(OH)$ (A. 270, 114).

Phenylhydrazine Sulphonic Acid, $C_6H_5NH.NH.SO_3H$.—The potassium salt is formed in the reduction of potassium benzene-diazosulphonate with sulphurous acid or monalkali sulphites. Consult p. 120 for the behavior of the potassium salt toward mineral acids, and the rôle it plays in the history of the discovery of phenylhydrazine.

p-**Nitrophenylhydrazine Disulphonic Acid,** $C_6H_4(NO_2)N(SO_3H)NH(SO_3H)$.—Its *dipotassium salt* consists of sulphur-yellow needles, formed on adding an excess of a sulphite solution to nitro-diazo benzene ester, nitrate, or isodiazobenzene potassium. Hydrochloric acid resolves it into p-nitrophenylhydrazine, and it dissolves in an excess of potash to a red *tripotassium salt*, $C_6H_4(NO_2)N(SO_3K)NK(SO_3K)$ (B. **29**, 1830).

Phenylbenzene Sulphazide, $C_6H_5NH.NH.SO_2C_6H_5$, melts with decomposition at 148–150°. It is formed from phenylhydrazine and benzene sulphochloride in ethereal solution, as well as from a diazobenzene salt solution by the action of sulphur dioxide (p. 120) (B. **20**, 1238). See A. 270, 123, for the action of PCl_3, $POCl_3$, $PSCl_3$, $AsCl_3$, BCl_3, $SiCl_4$ upon phenylhydrazine.

Carboxylic Acid Derivatives of Phenylhydrazine.—Acid residues of the most varied character can be as readily introduced into phenylhydrazine, and generally by the same methods, as into aniline. The domain of the bodies thus won from phenylhydrazine is scarcely less extensive than that of the acid derivatives of aniline, and in the multiplicity of phenomena really surpasses it.

The acid hydrazides and the hydrazido-acids have shown themselves to be as well adapted as the phenylhydrazones for the formation of heterocyclic derivatives. Each group of carboxylic derivatives of phenylhydrazine will be followed by the most important hetero-ring formations, arranged in tabular form, which will later be discussed in a different connection in the section devoted to "heterocyclic compounds."

The *amidrazones* and *formazyl derivatives* will receive attention at the conclusion of the simpler carboxylic derivatives of phenylhydrazine.

Fatty Acid Derivatives.—The fatty acid residues enter the amido-group of phenylhydrazine very readily with the production of sym.- or β-acidyl compounds. The unsym.- or α-acidyl-compounds are made (1) by the action of acid chlorides or anhydrides upon sodium phenylhydrazine (B. **22**, R. 664); (2) by action of suitable haloid derivatives upon β-acetylphenylhydrazine, and subsequent splitting-off of the β-acet group on boiling with dilute sulphuric acid, when the group occupying the α-position will not be attacked (B. **26**, 945).

The sym. phenylhydrazides, treated with ferric chloride and concentrated sulphuric acid, yield reddish to bluish violet colors, whereas the unsym.-bodies are not colored (B. **27**, 2965, Bülow's reaction).

sym.-*Formylphenylhydrazide*, $C_6H_5NH.NH.CHO$, from formic acid and phenylhydrazine, melts at 145° (B. **27**, 1522; **28**, R. 764).

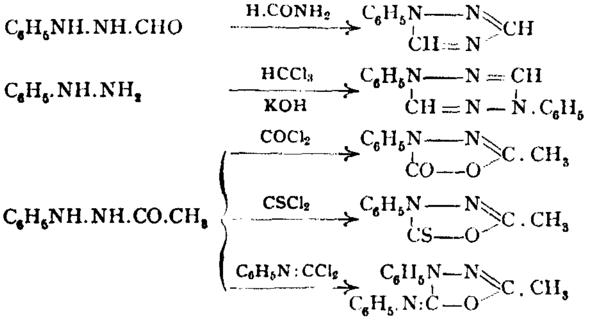
unsym.- or α-*Acetphenylhydrazide*, $C_6H_5N(COCH_3)NH_2$, from αβ-diacetphenyl-

hydrazine on heating with dilute sulphuric acid, melts at 124° (B. **27**, 2964). sym.- or *β-Acetphenylhydrazide*, $C_6H_5NH . NH . CO . CH_3$, melting at 128°, is obtained from phenylhydrazine with acetic anhydride, or upon boiling with glacial acetic acid (A. **190**, 129). *αβ-Diacetphenylhydrazide*, $C_6H_5N(CO . CH_3)NH . CO . CH_3$, melting at 106°, results when acetyl chloride acts upon potassium phenylhydrazine in ethereal solution (B. **20**, 47).

Hetero-ring Formations of the Fatty Acid Phenylhydrazide Derivatives:

n-*Phenyltriazole* results when formylphenylhydrazide is heated with formamide (B. **27**, R. 801). n-*Diphenylisodihydrotetrazine* is also a formic acid derivative of phenylhydrazine: It results from the action of chloroform and caustic potash upon phenylhydrazine (compare action of chloroform and caustic potash upon primary amines: I, 236, and II, 84, isonitriles or carbylamines).

The sym.- or *β*-acidylphenylhydrazides, treated with phosgene, thiophosgene, and isocyanphenyl chloride, yield heterocyclic compounds—the *oxybiazoline derivatives* (B. **26**, 2870), which can also be regarded as derivatives of carbonic acid:



n-Phenyltriazole

n-Diphenylisodihydrotetrazine

n-Phenyl-c-methyloxybiazolon

n-Phenyl-c-methylthio-oxybiazoline

n-Phenyl-c-methylphenylimido-oxybiazoline.

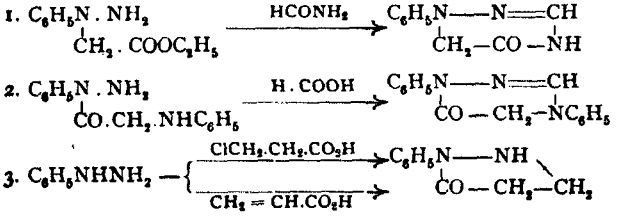
Alcohol Acid Derivatives of Phenylhydrazine.—sym.-*Phenylhydrazidoacetic acid*, $C_6H_5NH . NH . CH_2 . CO_2H$, melts at 158°; see vol. I, 360. unsym.-*Phenylhydrazidoacetic acid*, $C_6H_5N(NH_2)CH_2.CO_2H$, melting at 167°, is obtained by the careful saponification of its liquid ethyl ester, the reduction product from *nitrosophenylglycin ester*, $C_6H_5N(NO) . CH_2 . CO_2 . C_2H_5$ (B. **28**, 1223); its *phenylhydrazide*, melting at 178°, is formed from chloracetamide and phenylhydrazine (B. **29**, 622).

β-Phenylhydrazido-β-propionic Ester, $C_6H_5N(NH_2)CH_2 . CH_2 . CO_2 . C_2H_5$, boiling at 175° (9 mm.), is obtained from nitroso-*β*-anilidopropionic ester (B. **29**, 515).

β-Phenylhydrazido-β-butyric Acid, $C_6H_5N(NH_2) . CH(CH_3)CH_2COOH$, from *β*-chlorbutyric ester and phenylhydrazine, melts at 111° (J. pr. Ch. **45**, 87).

Hetero-ring Formations of the Phenylhydrazido-acids.—(1) Unsymmetrical phenylhydrazido-acetic ester condenses with formamide to *phenylketodihydro-a-triazine*. (2) *n-Diphenylketodihydro a-triazine* (see below) is similarly obtained from unsym.-*anilidoacetic acid-a-phenylhydrazide*, $C_6H_5N(NH_2)CO . CH_2 . NHC_6H_5$.

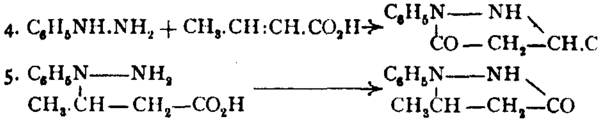
The phenylhydrazido-carboxylic acids (3, 4, 5) corresponding to the *β*-oxyacids show such readiness to anhydride (*pyrazolidone-* or *lactazam-*) formation that frequently it is impossible to isolate them:



n-Phenylketotetrahydro-*a*-triazine

n-Diphenylketotetrahydro-*a*-triazine

1-Phenyl-5-pyrazolidone



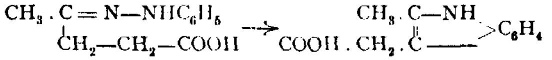
1-Phenyl-3-methyl-5-pyrazolidone

1-Phenyl-5-methyl-3-pyrazolidone.

Phenylhydrazine Derivatives of the Mono-ketonic Acids.—The α-, β-, and γ-ketone carboxylic esters react with phenylhydrazine, forming phenylhydrazones, just as the ketones do. The phenylhydrazones of α- and γ-ketone carboxylic acids are known. Zinc chloride or concentrated sulphuric acid rearranges the phenylhydrazones of the α-, β-, and γ-ketone carboxylic acids into indol derivatives (compare indol formation of the ketone phenylhydrazones, p. 124). The phenylhydrazones of the β- and γ-ketone carboxylic esters and of the free γ-ketone carboxylic esters manifest great tendency to the lactazam formation. *Lævulinic-phenylhydrazone* (1, 360) yields 1-*phenyl*-3-*methylpyridazinone* (see this), and under other conditions α-*methylindol*-β-*acetic acid*. *Acetoacetic Ester Phenylhydrazone*, $C_6H_5NH.N = C(CH_3).CH_2.CO_2C_2H_5$, melting at 50°, is formed on adding acetoacetic ester to phenylhydrazine (B. 27, R. 793), and spontaneously forms 1-*phenyl*-3-*methylpyrazolon* (see this); whereas with acetyl chloride or excessive hydrochloric acid it yields 1-*phenyl*-3-*methyl*-5-*ethoxypyrazole* (see this).

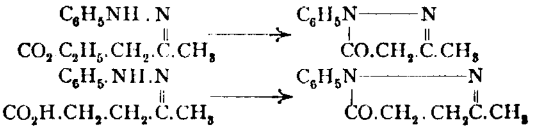
Hetero-ring Formations of the Phenylhydrazone-ketonic Acids.

1. *Indol* condensation (see p. 124):



α-Methylindol-β-acetic Acid

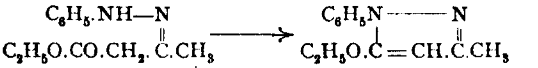
2. *Lactazam* formation:



1-Phenyl-3-methyl-5-pyrazolon

1-Phenyl-3-methylpyridazinone

3. *Pyrazole* formation:



1-Phenyl-3-methyl-ethoxypyrazole.

Phenylhydrazine Derivatives of Carbonic Acid.—*Phenylhydrazine Phenylcarbazinate*, $C_6H_5NH.NH.COONH_3NHC_6H_5$, is produced on saturating an aqueous emulsion of phenylhydrazine with carbonic acid. It is a white crystalline mass (B. 190, 123). *Ethyl Phenylcarbazinate*, $C_6H_5NHNHCOOC_2H_5$, melting at 86°, is produced when chlorcarbonic ester acts upon an ethereal phenylhydrazine solution. When it is heated to 240° it loses alcohol and becomes *diphenylurazine* (A. 263, 278; B. 26, R. 20). unsym.-*Phenylhydrazido-formic Ester*, $C_6H_5N(NH_2)CO\text{-}OC_2H_5$, is an oil, obtained from its *acet*-derivative, which results from the interaction of acetphenylhydrazine and chlorformic ester (B. 29, 829).

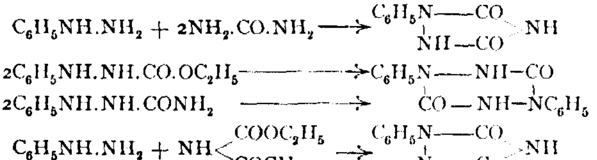
Phenylsemicarbazide, $C_6H_5NH.NH.CONH_2$, melting at 172°, is obtained from phenylhydrazine salts and potassium cyanate (A. 190, 113), or upon heating phenylhydrazine with urea or urethane. When heated it becomes phenylurazole and diphenylurazine, with the formation of CO, CO_2, NH_3, and benzene (B. 21, 1224). Phenylsemicarbazide, like sym.-acetphenylhydrazine (p. 125), is transposed by $COCl_2$, $CSCl_2$, and $C_6H_5NCCl_2$ into *oxybiazolon*-derivatives (B. 26, 2870). It forms benzeneazocarbonamide when its *nitroso*-compound (p. 131) is oxidized.

Diphenylcarbazide, $(C_6H_5.NH.NH)_2CO$, melting at 151°, results upon heating urethane with phenylhydrazine (B. 20, 3372) (compare B. 29, R. 982). A *dicarbox-*

ethyldiphenylcarbazide, $(C_6H_5NCO_2C_2H_5 . NH)_2CO$, melting at 19°, results from the action of $COCl_2$ upon unsym.-phenylhydrazidoformic ester (B. **29**, 829).

Cyclic Urea and Carbamic Acid Derivatives: Phenylurazole is produced on heating phenylsemicarbazide, or phenylhydrazine hydrochloride with urea, or biuret with phenylhydrazine. *Diphenylurazine* results upon heating ethylphenylcarbazinate and phenylsemicarbazide (A. **263**, 582).

1-*Phenyl*-3-*methyl*-5-*triazolon* is obtained from acetyl urethane and phenylhydrazine (B. **22**, R. 737).



Phenylurazole

Diphenylurazine

1-Phenyl-3-methyl-5-triazolon.

Phenylhydrazine Derivatives of Thiocarbonic Acid.—On mixing an ethereal solution of phenylhydrazine with carbon disulphide, *Phenylhydrazine Phenylsulphocarbazinate*, $C_6H_5NH . NH . CSSNH_3NHC_6H_5$, results. It melts at 96°. Mineral acids liberate the acid from solutions of salts of phenylsulpho-carbazinic acid. It separates in delicate, shining leaflets, which readily oxidize to the corresponding disulphide (A. **190**, 114). When the potassium salt of the acid is treated with $COCl_2$, CS_2, and ethylene bromide, the products are: n-*phenylthiobiazolonsulphydrate*, n-*phenyldithiobiazoline sulphydrate*, and n-*phenylthiopentahydrodiazthine* (B. **27**, 2516).

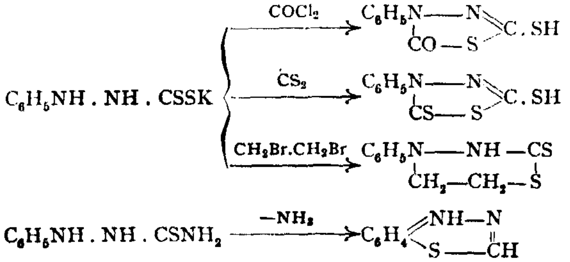
Phenylsulphosemicarbazide, $C_6H_5NH . NH . CSNH_2$, melting at 200°, is obtained from phenylhydrazine rhodanate at 160–170°. When heated to 130° with hydrochloric acid, it becomes *sulphocarbizine* or benzodiazthine (see this) (B. **27**, 871). *Diphenylsulphosemicarbazide*, $C_6H_5NH . NH . CS . NHC_6H_5$, from diphenylcarbazinic acid and aniline (B. **29**, 1686), is converted by nitrous acid into *diphenylisotetrazolon* (see this).

Diphenylsulphocarbazide, $(C_6H_5NH . NH)_2CS$, melting at 150°, is formed when phenylhydrazine phenylsulphocarbazinate is heated to 100–110°.

Diphenylsulphocarbazone, $C_6H_5N = N . CSNH . NH . C_6H_5$, consists of bluish-black crystals, and is formed by brief boiling of diphenylsulphocarbazide with moderately concentrated alcoholic potash.

Diphenylsulphocarbodiazone, $(C_6H_5N = N)_2CS$, from diphenylsulphocarbazone by oxidation with hydrated manganese peroxide, consists of red needles (A. **212**, 316).

Hetero-ring Formations of the Phenylhydrazine Thiocarbonic Acid Derivatives:



n-Phenylthiobiazolon-sulphydrate

n-Phenyldithiobiazoline sulphydrate

n-Phenylthiopentahydrodiazthine

Phenylsulphocarbizine Benzenediazthine.

Phenylhydrazine Derivatives of Guanidine.—*Anil Guanidine*, $NH : C(NH_2) . NHNHC_6H_5$, and *Amidophenyl guanidine*, $NH : C(NH_2) . N(C_6H_5)NH_2$, are formed together from cyanamide and phenylhydrazine (B. **29**, R. 1109); under other conditions the product is a phenylhydrazine derivative of *biguanide*—the easily decomposable *Anilbiguanide*, $C_6H_5NH . NH . C : (NH) . NH . C : (NH) . NH_2$. On digesting anil-

biguanide with cyanamide it changes to *phenylguanazole* (see this), which is obtained from *dicyandiamide* and phenylhydrazine (B. **24**, R. 649):

n-Phenylguanazole.

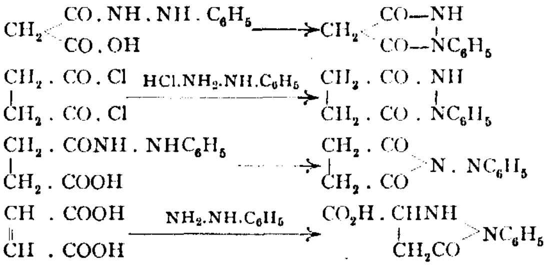
Phenylhydrazine Derivatives of the Dicarboxylic Acids.—*Oxalphenylhydrazilic Acid*, $C_6H_5NH.NH.CO.CO_2H$, melting at 110° (A. 236, 197), and *Oxalphenylhydrazide*, $(C_6H_5NH.NH.CO)_2$ melting at 278°, correspond to *oxanilic acid* and *oxanilide*.

Malonic acid has given the following phenylhydrazine derivatives: *Malonic Ester Phenylhydrazide*, Malonphenylhydrazilic ester, $C_6H_5NH.NH.CO.CH_2.COOC_2H_5$, melting at 90°, is produced when phenylhydrazine acts upon the chloride of malonic ester. It dissolves quite readily in caustic potash and from this solution hydrochloric acid precipitates *malonylphenylhydrazide*, 1-phenyl-3,5-pyrazolidone (formula below).

Malonylphenylhydrazide, $(C_6H_5NH.NH.CO)_2CH_2$, melting at 187°, results from the interaction of malonamide and phenylhydrazine at 200° (B. **25**, 1505). *Ethylene succinic acid* has yielded the compounds corresponding to those from malonic acid. *Succinic phenylhydrazilic ester* melts at 107°. *Succinylphenylhydrazine* results from the interaction of phenylhydrazine hydrochloride and succinyl chloride (B. **26**, 2181). *Succinyldiphenylhydrazide*, $(CH_2.CO.NH.NH.C_6H_5)_2$, melts at 209° (B. **21**, 2462). *Anilsuccinimide*, $(CH_2CO)_2NNHC_6H_5$, belongs in this category.

Phenylhydrazine Derivatives of Olefine Dicarboxylic Acids and Oxydicarboxylic Acids.—Maleïc anhydride and phenylhydrazine yield *maleïnphenylhydrazil*. On boiling maleïc or fumaric acid, dissolved in water, with an excess of phenylhydrazine, it adds itself as in the case of acrylic or crotonic acid (p. 126), and after the addition lactazam-formation ensues (B. **26**, 117), and *1-phenyl-5-pyrazolidon-3-carboxylic acid* results (see this).

Hetero-ring Formations of the Phenylhydrazine Derivatives of the Dicarboxylic Acids:



Malonylphenylhydrazine, 1-Phenyl-3,5-pyrazolidone

Succinylphenylhydrazine

Anilsuccinimide

1-Phenyl-5-pyrazolidon-3-carboxylic Acid.

HYDRAZIDINES OR AMIDRAZONES. FORMAZYL COMPOUNDS.

Two classes of compounds belonging to the amidines remain to be discussed at the conclusion of the phenylhydrazine derivatives of the carboxylic acids. The hydrazidines are amidines whose imido-group is replaced by the phenylhydrazone group, while in the formazyl compounds the amido-group is in addition replaced by the azophenyl group:

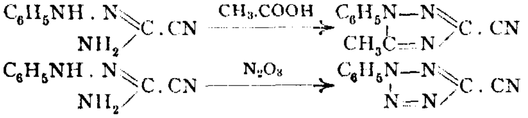
Acetamidine	Ethenylphenylhydrazidine	Formamidine	Formazyl Hydride.
$CH_3.C\begin{smallmatrix}NH_2\\NH\end{smallmatrix}$	$CH_3.C\begin{smallmatrix}NH_2\\N.NHC_6H_5\end{smallmatrix}$	$HC\begin{smallmatrix}NH_2\\NH\end{smallmatrix}$	$HC\begin{smallmatrix}N{=}NC_6H_5\\N{-}NHC_6H_5\end{smallmatrix}$

A. **Hydrazidines or Amidrazones.** *Ethenylphenylhydrazidine*, $CH_3.C\begin{smallmatrix}N.NHC_6H_5\\NH_2\end{smallmatrix}$.
The hydrochloride of this base is produced by the action of phenylhydrazine upon the

hydrochloride of acetimidoether (B. 17, 2002). *Cyanamidrazone* or *Dicyanphenylhydrazine*, $NC{-}C\begin{smallmatrix}{\nearrow}N.NH.C_6H_5\\ {\searrow}NH_2\end{smallmatrix}$, melting with decomposition at 160°, and *Diamidrazone* (B. 26, 2783 Anm.), or *Cyanphenylhydrazine*, $\left(\begin{smallmatrix}C_6H_5NH.N{\searrow}\\ NH_2{\nearrow}\end{smallmatrix}C\right)_2$, melting at 225°, are produced when cyanogen acts upon phenylhydrazine. Dicyanphenylhydrazine is formed by the reduction of the HCN addition product of diazobenzene cyanide (p. 103), which probably, therefore, has the following formula: $C_6H_5N:NC\begin{smallmatrix}{\nearrow}NH\\ {\searrow}CN\end{smallmatrix}$ (B. 28, 2082). The constitution of cyanamidrazone is evident from its formation through the action of phenylhydrazine upon *Flaveanhydride*, $NC{-}C\begin{smallmatrix}{\nearrow}S\\ {\searrow}NH_2\end{smallmatrix}$, and the constitution of diamidrazone from its formation in the action of phenylhydrazine upon *Rubeanhydride*, $\begin{smallmatrix}S{\searrow}\\ NH_2{\nearrow}\end{smallmatrix}C{-}C\begin{smallmatrix}{\nearrow}S\\ {\searrow}NH_2\end{smallmatrix}$ (1, 437), and upon oxaldiamidoxime, $\begin{smallmatrix}HON{\searrow}\\ NH_2{\nearrow}\end{smallmatrix}C{-}C\begin{smallmatrix}{\nearrow}NOH\\ {\searrow}NH_2\end{smallmatrix}$ (B. 26, 2385).

Acetylamidrazone, pyroracemic acid phenylhydrazidine, $CH_3CO.C\begin{smallmatrix}{\nearrow}N.NHC_6H_5\\ {\searrow}NH_2\end{smallmatrix}$, melting at 182°, is produced by reducing formazyl methylketone with ammonium sulphide (B. 26, 2783).

Hetero-ring Formations with the Amidrazones.—The amidrazones condense with carboxylic acids, their anhydrides or chlorides to hetero-cyclic derivatives of the *triazole*-group (see this). Nitrous acid converts the amidrazones into *tetrazole*-derivatives (see these). Cyanamidrazone is changed by acetic anhydride to n-*phenyl*-3-*cyan*-5-*methyltriazole*; by nitrous acid to n-*phenyl*-3-*cyantetrazole*:



n-Phenyl-3-cyan-5-methyltriazole

n-Phenyl-3-cyan-tetrazole.

B. **Formazyl compounds** are obtained (1) from phenylhydrazones and normal diazobenzene usually in alkaline solution; (2) from phenylhydrazine and phenylhydrazides; the hydrazone-hydrazide produced at first oxidizes, under the influence of phenylhydrazine, with the loss of two hydrogen atoms; (3) from the phenylhydrazone chlorides, corresponding to the imide chlorides, by action of phenylhydrazine (B. 27, 320; 29, 1386).

Formazyl Hydride, $HC\begin{smallmatrix}{\nearrow}N:NC_6H_5\\ {\searrow}N.NHC_6H_5\end{smallmatrix}$, melting at 116° (1, 233), has been obtained from formazyl carboxylic acid by fusing it alone, or by boiling it with alcoholic potash.

Formazyl Methyl Ketone, $CH_3.CO.C\begin{smallmatrix}{\nearrow}N:NC_6H_5\\ {\searrow}N.NHC_6H_5\end{smallmatrix}$, melting at 134°, results from the action of diazobenzene upon acetone, acetoacetic ester, pyroracemic aldehyde hydrazone, and benzene-azo-acetyl acetone (B. 25, 3211).

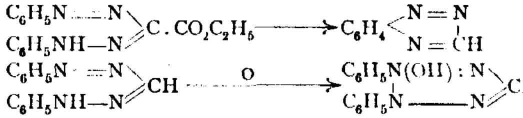
Formazyl Carboxylic Acid, $CO_2H.C\begin{smallmatrix}{\nearrow}N:N_6H_5\\ {\searrow}N.NH.C_6H_5\end{smallmatrix}$, melting at 162°, is made by saponifying the ethyl formazyl carboxylic ester, melting at 117°. The latter is produced when diazobenzene chloride acts upon acetoacetic ester, oxaloacetic ester (B. 25, 3456), or upon phenylhydrazone-mesoxalic ester acid. *Diformazyl*,

$$\begin{smallmatrix}C_6H_5N:N{\searrow}\\ C_6H_5NH.N{\nearrow}\end{smallmatrix}C.C\begin{smallmatrix}{\nearrow}N:NC_6H_5\\ {\searrow}N.NHC_6H_5\end{smallmatrix},$$

greenish-brown, brilliant leaflets, melting at 226°. It results from the action of diazobenzene chloride upon lævulinic acid, hydrochelidonic acid, or acetone diacetic acid, and from dioxytartrosazone.

Formazylazobenzene, Phenylazoformazyl, $(C_6H_5N = N)_2C = N . NHC_6H_5$, melting at 162°, results from the interaction of formazyl carboxylic acid or glyoxylic acid phenylhydrazone and diazobenzene in alkaline solution (B. **25**, 3457).

Hetero-ring Formations with the Formazyl Derivatives.—When concentrated mineral acids act upon the formazyl compounds, they split off aniline and *phentriazone* derivatives result; formazyl carboxylic ester yields *a-Phentriazine* (see this). By oxidation the formazyl-compounds change to *tetrazolium* derivatives; formazyl hydride yields n-*Diphenyltetrazolium hydroxide*:



a-Phentriazine

n-Diphenyltetrazolium Hydroxide.

16. **Phenylnitrosohydrazine,** $C_6H_5N{<}{}^{NO}_{NH_2}$, or $C_6H_5NHNHNO$, yellowish-brown crystalline flakes, which readily change to diazobenzene imide (p. 110) (A. **190**, 89), and are produced by action of nitrous acid upon phenylhydrazine. An excess of nitrous acid oxidizes phenylhydrazine to a diazobenzene salt (Ch. C. 1897, I, 381). *Nitrosophenylsemicarbazide*, $C_6H_5N(NO)NHCONH_2$, melting with decomposition at 127°, is obtained by the action of NO_2Na and acetic acid upon phenylsemicarbazide. It decomposes gradually at the ordinary temperature, more rapidly upon heating, with the production of phenylazocarbamide (p. 103). Diazobenzeneimide is obtained when it is boiled with caustic potash (B. **28**, 1925).

16*a*. **Tetrazones,** derived from the hypothetical nitrogen hydride, $NH_2 — N = N — NH_2$, result upon oxidizing the unsym.-alkylphenyl- or diphenyl-hydrazines with mercuric oxide in alcoholic or ethereal solution, or by means of a dilute ferric chloride solution:

$$2C_6H_5N(CH_3) . NH_2 + 2O = C_6H_5 . N(CH_3) . N : N . N(CH_3) . C_6H_5 + 2H_2O.$$

They are solids, decomposed by fusion or upon boiling with dilute acids. *Dimethyl diphenyl Tetrazone*, $C_6H_5 . N(CH_3)N_2 . N(CH_3)C_6H_5$, melts at 133°. *Diethyldiphenyl Tetrazone* melts at 108° (A. **252**, 281). *Tetraphenyl Tetrazone*, $(C_6H_5)_2N . N_2 . N(C_6H_5)_2$, from a-diphenylhydrazine, melts at 123°, and is colored blue by concentrated acids. The tetrazones recall the osotetrazones (I, 328).

16*b*. **Hydrotetrazones,** derived from the hypothetical hydride, $NH_2 . NH . NH . NH_2$, result upon oxidizing the aldehyde phenylhydrazones (B. **26**, R. 55; **27**, 2920)—*e.g.*, benzal phenylhydrazone yields the compound, $\begin{array}{l} C_6H_5 . CH : N . N . C_6H_5 \\ C_6H_5 . CH : N . N . C_6H_5 \end{array}$, *dibenzal diphenyldihydrotetrazone*, melting at 181° (B. **29**, R. 591).

17. **Buzylene or Diazohydrazo-compounds.**—*Hippurylphenylbuzylene*, $C_6H_5N = N — NH — NHCO . CH_2 . NH . CO . C_6H_5$, melting at 84°, is an hippuric acid derivative of the unknown hydride, *Buzylene*, $NH = N — NH — NH_2$ (B. **26**, 1268). It is formed from hippurylhydrazine and diazobenzene sulphate.

4. AROMATIC COMPOUNDS OF PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH, BORON, SILICON, AND TIN (I, 173–181).

The phenyl-derivatives of the elements just mentioned attach themselves to the aromatic nitrogen compounds. Their chlorides are most suitable for the preparation of these bodies. (1) They react with benzene at a red heat. hydrochloric acid being eliminated; (2) with benzene and aluminium chloride; (3) with mercury diphenyl; (4) with sodium and benzene chloride, or benzene bromide. This class of derivatives is produced also (5) from alloys of the elements with alkali metals and benzene haloids.

Phenyl Phosphorus Compounds.—Michaelis in 1876 succeeded, by the preparation of phosphenyl chloride, the starting-out substance for the obtainment of phosphenyl derivatives, in setting aside the experimental difficulties which opposed the union of the phenyl residue with phosphorus (A. 181, 265; 293, 193, 325; 294, 1). Some phosphenyl compounds in composition correspond to known aromatic nitrogen-containing substances; the names of the respective phosphenyl bodies recall these:

Aniline,	$C_6H_5NH_2$	$C_6H_5PH_2$,	Phenylphosphine
Nitrobenzene,	$C_6H_5NO_2$	$C_6H_5PO_2$,	Phosphino-benzene
Azobenzene,	$C_6H_5N : NC_6H_5$	$C_6H_5P : PC_6H_5$,	Phospho-benzene.

Phenylphosphine, $C_6H_5 . PH_2$, phosphaniline, boiling at 160°, is obtained by the action of hydriodic acid and then alcohol upon phosphenyl-chloride, $C_6H_5 . PCl_2$. It is a liquid possessing an extremely disagreeable odor. When exposed to the air, it oxidizes to phosphenyl oxide, $C_6H_5 . PH_2O$,—a crystalline mass easily soluble in water. Phenylphosphine combines with HI to the iodide, $C_6H_5 . PH_3I$, out of which water again separates phenylphosphine.

Phosphenyl Chloride, $C_6H_5 . PCl_2$, boiling at 225° (corr.) with sp. gr. 1.319 (29°), is a strongly refracting liquid which fumes in the air. It is formed (1) by conducting a mixture of benzene and PCl_3 vapors through tubes heated to redness (A. 181, 280); (2) by heating mercury diphenyl with PCl_3, and (3) by the action of $AlCl_3$ upon benzene and PCl_3. Aided by this last reaction the chlorphosphin-residue has also been introduced into *dimethylaniline* (B. 21, 1497), and into *phenolalkyl ether* (B. 27, 2559). It forms the *tetrachloride*, $C_6H_5 . PCl_4$, with chlorine; this melts at 73°. With oxygen it yields the *oxychloride*, $C_6H_5 . PCl_2O$, boiling at 260°, and with sulphur *phosphenyl sulpho-chloride*, boiling at 205° (130 mm.). When the dichloride is heated with water, we obtain phenyl-hypophosphorous acid, $C_6H_5 . PHO . OH$, melting at 70°, while the tetrachloride forms phenylphosphinic acid, $C_6H_5 . PO . (OH)_2$, which melts at 150°.

p-*Tolylphosphorchloride*, $CH_3[4]C_6H_4PCl_2$, forms a tetrachloride, which forms with aniline *tolyltrianilidophosphonium chloride*, $CH_3[4]C_6H_4P(NHC_6H_5)_3Cl$, melting at 245°. Sodium hydroxide converts the latter into the *hydroxide*, $CH_3C_6H_4P(NHC_6H_5)_3OH$, melting at 240° (B. 28, 2214).

Phosphino-benzene, $C_6H_5PO_2$, melting at 100°, is obtained from phosphenyloxychloride and phenylhypophosphorous acid (B. 25, 1747).

Phosphenyl chloride converts phenylphosphine into **Phospho-benzene,** $C_6H_5 . P : P . C_6H_5$, melting at 150° (B. 10, 812).

Diphenylphosphine Chloride, $(C_6H_5)_2PCl$, boiling at 320°, is obtained from phosphenyl chloride alone at 280°, or with mercury diphenyl at 220° (B. 21, 1505). With phenol it yields *Phenoxyldiphenylphosphine*, $(C_6H_5)_2POC_6H_5$, boiling at 265–270° (62 mm.) (B. 18, 2118), and with dilute sodium hydroxide: *diphenylphosphine*, $(C_6H_5)_2PH$, boiling at 280°, and *diphenylphosphinic acid*, $(C_6H_5)_2PO . OH$, melting at 190° (B. 15, 801).

Triphenylphosphine, $(C_6H_5)_3P$, melting at 75° and boiling about 360°, is produced from $C_6H_5 . PCl_2$, and brombenzene, or from PCl_3 and brombenzene by the action of sodium (B. 18, R. 562). It forms, with bromine, the dibromide, $(C_6H_5)_3PBr_2$, which is converted by water or alkalies into the dihydroxide, $(C_6H_5)_3P(OH)_2$. At 100° this passes into the oxide, $(C_6H_5)_3PO$. The latter melts at 143° and boils above 360°. **Triphenylphosphin-oxide,** $(C_6H_5)_3PO$, is isomeric with *phenoxyldiphenylphosphine*, $(C_6H_5)_2POC_6H_5$. Both compounds, in vapor density determinations made with reduced pressure (1, 29), yield values according with the simple molecular formulas. Phosphorus, therefore, in the first body is quinquivalent, and in the second it is trivalent (Michaelis and La Coste, B. 18, 2118).

Phenyl Arsenic Compounds.—Reactions similar to those used in obtaining the phenyl substitution products of phosphorous chloride have been used with arsenic, and the following bodies have been obtained: *Phenyl arsenious chloride*, $C_6H_5AsCl_2$; *Diphenyl arsenious chloride*, $(C_6H_5)_2AsCl$; *Triphenyl Arsine*, $(C_6H_5)_3As$; *Arsenobenzene*, $C_6H_5As : As . C_6H_5$. (A. 201, 191; 207, 195; 270, 139; B. 19, 1031; 25, 1521; 27, 263).

Triphenyl Stibine, $(C_6H_5)_3Sb$, melting at 48°, is produced on introducing sodium

into a solution of 40 grams of chlorbenzene and 40 grams of antimonious chloride in benzene (A. 233, 43).

Bismuth Triphenyl, $(C_6H_5)_3Bi$, melting at 78°, is prepared by heating brombenzene and bismuth sodium (A. 251, 324).

Phenyl Boron Compounds.—*Phenyl boron chloride*, $C_6H_5BCl_2$, melting at 0° and boiling at 175°, and *diphenylboron-chloride*, $(C_6H_5)_2BCl$, boiling at 271° (B. 27, 244), result from the interaction of mercury diphenyl and boron chloride.

Phenyl Silicon Compounds.—Phenyl-silico-chloride, $C_6H_5 . SiCl_3$, is prepared by heating mercury diphenyl and $SiCl_4$ to 300°. It boils at 197° (Ladenburg, A. 173, 151). Water decomposes it into silico-benzoic acid, $C_6H_5 . SiO . OH$, melting at 92°. Alcohol forms the triethyl ether, $C_6H_5 . Si(O . C_2H_5)_3$, boiling at 137°. Zinc ethyl converts the chloride into *triethyl-phenyl-silicide*, $C_6H_5 . Si . (C_2H_5)_3$, boiling at 230°.

* **Tetraphenyl Silicon**, $Si(C_6H_5)_4$, is produced by the action of sodium upon a mixture of $SiCl_4$, chlorbenzene, and ether (B. 19, 1012). It melts at 228° and distils beyond 300°.

Phenyl Tin Compounds.—Mercury diphenyl and stannic chloride interact to form **Tin Diphenyl Chloride**, $(C_6H_5)_2SnCl_2$, melting at 42° (A. 194, 145).

Tin Tetraphenyl, $Sn(C_6H_5)_4$, is produced by the action of tin sodium upon brombenzene. It melts at 226° and boils above 420° (B. 22, 2917).

5. PHENYL METAL DERIVATIVES (1, 182).

The phenyl group has been combined with magnesium, mercury, and lead.

Magnesium Diphenyl, $(C_6H_5)_2Mg$, is a light, yellowish-white powder, dissolving readily in a mixture of benzene and ether. It is produced on heating mercury diphenyl with magnesium powder and some acetic ester to 180–185° (A. 282, 320).

Mercury-phenyl, $(C_6H_5)_2Hg$, melting at 120°, is formed by treating brombenzene in benzene solution for some time with liquid sodium amalgam (Otto and Dreher, A. 154, 93); the addition of some acetic ether facilitates the reaction. It crystallizes in colorless, rhombic prisms, and can be sublimed. It assumes a yellow color in sunlight. It dissolves readily in benzene and carbon disulphide, but with more difficulty in ether and alcohol; in water it is insoluble. When distilled it decomposes for the most part into diphenyl, benzene, and mercury. Acids decompose it with formation of benzene and mercury salts. Haloid compounds are produced by the action of the halogens—*e.g.*, *Mercury-phenyl chloride*, C_6H_5HgCl, melting at 250°; *mercury-phenyl bromide*, C_6H_5HgBr, melting at 275°; *mercury-phenyl iodide*, C_6H_5HgI, melting at 265°. *Mercury-phenyl hydroxide*, C_6H_5HgOH, is produced when silver oxide and alcohol act upon the chloride (J. pr. Ch. [2] 1, 186).

Mercury Dialphyls: See A. 173, 162; B. 14, 2112; 17, 2374; 20, 1719; 22, 1220, etc.

Lead Tetraphenyl, $(C_6H_5)_4Pb$, is formed by heating brombenzene with lead sodium and acetic ether. It melts at 224° (B. 20, 3331).

6. SULPHO-ACIDS.

The ease with which sulpho-acids are produced distinguishes the aromatic hydrocarbons from the aliphatic bodies to the same degree that marks their easy nitration. The introduction of a sulpho-group in the place of aromatic hydrogen atoms is termed "sulphonation."

Formation.—(1) The ***sulphonic acids*** of the benzene hydrocarbons (as well as of other benzene derivatives) are very easily obtained by mixing (or digesting) the latter with concentrated or fuming sulphuric acid. In

this manner it is possible to combine three sulpho-groups with one benzene nucleus:

$$C_6H_6 + HO.SO_3H = C_6H_5.SO_3H + H_2O.$$

(2) In the action of an excess of chlorsulphonic acid, $Cl.SO_2OH$, the principal products, with careful cooling, are the chlorides of the sulpho-acids (B. **12**, 1848; **28**, 2172). The reaction then proceeds in the following way (B. **22**, R. 739):

$$C_6H_6 + ClSO_2OH = HCl + C_6H_5.SO_2OH$$
$$C_6H_5SO_2OH + ClSO_2OH = H_2SO_4 + C_6H_5SO_2Cl.$$

Sulphones are secondary products (p. 139).

(3) Further, sulphonic acids can be obtained from the diazo-amido-derivatives by boiling with sulphurous acid (p. 110).

(4) By the oxidation of thiophenols (p. 156). This reaction proves that the sulphur atom of the sulpho-group is in union with the aromatic nucleus (compare mercaptans) (1, 148).

(5) By the oxidation of sulphinic acids (p. 138).

Properties and Transformations.—Many aromatic sulpho-acids are very soluble in water and crystallize with difficulty. They can be separated from aqueous solution in the form of their sodium salts by means of sodium chloride: *salting out* (B. **28**, 91). The ready solubility of the sulpho-acids, in conjunction with their easy production, meets with an important technical application in the conversion of aromatic dyes insoluble in water into their sulpho-acids, which dissolve in water with ease.

(1) The chlorides of the acids are made by acting upon the alkali salts with $POCl_3$ and PCl_5, and from the acids themselves by the action of PCl_5. The chlorides are converted into amides, esters, etc., as indicated under the alkyl sulphonic acids (1, 152). The esters of the sulpho-acids are transposed by alcohol at 140–150°, with the production of ethers (1, 133). The sulphonamides are stable and crystallize well; they are frequently prepared for the characterization of a sulpho-acid.

(2) Hydrocarbons (together with phenyl sulphones) are formed when the free acids are subjected to distillation:

$$C_6H_5.SO_3H = C_6H_6 + SO_3.$$

This rupture is more easily accomplished by heating the acids with concentrated HCl to 150°, or by distilling the ammonium salt of the sulphonic acid, or a mixture of the lead salt with ammonium chloride (B. **16**, 1468). The decomposition results with least difficulty by conducting steam into the dry sulpho-acid, or its solution in concentrated sulphuric acid; superheated steam is most effective (B. **19**, 92).

(3) The SO_2Cl group in the sulpho-chlorides can be replaced by chlorine through the action of PCl_5. In some sulphonic acids free chlorine and bromine are capable of eliminating the sulpho-group and introducing the halogens (B. **16**, 617).

(4) The sulpho-group in many sulphonic acids is often replaced by NO_2 upon treating them with concentrated nitric acid.

(5) Anilines result from the action of sodamide, NH_2Na, upon benzene sulphonates (B. **19**, 903):

$$C_6H_5.SO_3Na + NH_2Na = C_6H_5.NH_2 + SO_3Na_2.$$

(6) The sulphonic acids of the alkyl benzenes, more frequently applied in the form of their sulphamides, yield sulphocarboxylic acids upon oxidation. The oxidation of o-toluene sulphamide to the sulphinide of o-sulphobenzoic acid (see this), called *saccharin*, is technically important.

(7) The chlorides of the aromatic sulpho-acids become thiophenols upon reduction:

$$C_6H_5SO_2Cl + 6H = C_6H_5SH + 2H_2O + HCl.$$

This reaction, like that of the oxidation of thiophenols to sulphonic acids, demonstrates that in the sulpho-acids the sulphur is in immediate union with the benzene nucleus

(8) The sulphonic acids are not decomposed upon boiling them with aqueous alkalies. Phenols are formed when they are fused with alkalies. This reaction serves for the technical preparation of resorcinol (p. 160) and other phenols:

$$C_6H_5.SO_3K + KHO = C_6H_5OH + SO_3K_2.$$

(9) When distilled with potassium cyanide (or dry yellow prussiate of potash) nitriles result:

$$C_6H_5.SO_3K + CNK = C_6H_5.CN + SO_3K_2,$$

and these may be readily saponified to carboxylic acids. This reaction answers for the synthesis of aromatic acids from the hydrocarbons.

(10) Carboxylates are also obtained on fusing the alkali sulphonates with sodium formate.

Monosulphonic Acids.—**Benzene Sulphonic Acid,** $C_6H_5.SO_3H$, melting at 50°, crystallizes from water, in which it is exceedingly soluble, in plates containing water of crystallization.

The *barium salt*, $(C_6H_5.SO_3)_2Ba + H_2O$, forms pearly leaflets, and is sparingly soluble in alcohol.

The **chloride**, $C_6H_5.SO_2Cl$, melts at 14.5°, boils at 116° (B. 25, 2257), and has specific gravity of 1.378 at 23°. It slowly reverts to the acid upon boiling with water. The *ethyl ester*, boiling at 156° (15 mm.), obtained by the action of ethyl alcohol on the chloride, is decomposed into benzene sulphonic acid and ethyl ether (1, 133) when it is heated to 150° with ethyl alcohol.

Benzenesulphamide, $C_6H_5.SO_2.NH_2$, melts at 150°.

Benzene Sulpho-nitramide, $C_6H_5SO_2NHNO_2$, consists of colorless plates, readily soluble in water. It decomposes at 100° into benzene sulphonic acid and nitrous oxide. It is formed when a mixture of nitric and sulphuric acids acts upon benzenesulphamide. Its *potassium salt*, $C_6H_5SO_2NK.NO_2$, melts at 275°, and when reduced by glacial acetic acid and zinc dust becomes *benzene sulphon-hydrazide*, $C_6H_5SO_2NH.NH_2$. The sulphamide and nitrous acid yield *dibenzene sulphon-hydroxylamine*, $(C_6H_5SO_2)_2NOH$, which can also be made by the interaction of benzene sulphinic acid and sodium nitrite; with diazobenzene chloride the product is *benzene sulpho-diazobenzene amide*, $C_6H_5SO_2NH—N=N.C_6H_5$, melting with decomposition at 101° (B. 27, 598).

Benzsulph-hydroxamic Acid, $C_6H_5SO_2.NHOH$, melting at 126°, is obtained from benzene sulphochloride and hydroxylamine. Alkalies decompose it into benzene sulphinic acid and hyponitrous acid (B. 29, 1559, 2324):

$$2C_6H_5SO_2NHOH + 2KOH = 2C_6H_5SO_2K + (NOH)_2 + 2H_2O.$$

Toluene Sulphonic Acids.—In sulphonating toluene o- and p-acids are the chief products. The o-acid can be obtained from p-tolylhydrazine-o-sulphonic acid free from the p-acid. The m-acid is obtained from p-toluidine-m-sulphonic acid. o-*Toluene Sulphochloride* is a liquid. o-*Toluene-sulphamide* melts at 155° (see o-sulphobenzoic acid). m-*Toluene-sulphonic Acid*, $CH_3[1]C_6H_4[3]SO_3H + H_2O$; its *chloride* is a liquid; its *amide* melts at 107°. p-*Toluene-sulphonic Acid*, $CH_3[1]C_6H_4[4]SO_3H + 4H_2O$, melts at 92°; its *chloride* melts at 69° and boils at 145° (15 mm.); its *bromide* melts at 96°, its *iodide* at 84°, and its *amide* at 137°. *Ditoluene sulph-hydroxamic acid*, $(C_7H_7.SO_2)_2NOH$, melts with decomposition at 148°. It results from the action of

sodium nitrite upon toluene-sulphinic acid. It combines with an additional molecule of the sulphinic acid to *Tritoluene Sulphonamide*, $(C_7H_7 . SO_2)_3N$, melting at 190° (J. pr. Ch. [2] 54, 95).

Xylene Sulphonic Acids.—1,2-*Xylene-4-sulphonic Acid;* its *chloride* melts at 51°, its *amide* at 144°. 1,3-*Xylene-4-sulphonic Acid*; its *chloride* melts at 34° and its *amide* at 137°. 1,3-*Xylene-2-sulphonic Acid:* its *amide* melts at 95°. 1,4-*Xylene-3-sulphonic Acid:* its *chloride* melts at 25° and its *amide* at 247°. They result upon sulphonating the various xylenes.

[1,2,4]-*Pseudocumene-5-sulphonic Acid*, $(CH_3)_3C_6H_2SO_3H + 2H_2O$, melts at 111°. Its *chloride* melts at 61° and the *amide* at 181°. *Mesitylene Sulphonic Acid*, $C_9H_{12}SO_3 + 2H_2O$, melts at 77°, its *chloride* at 57°, and its *amide* at 141°.

Polysulphonic Acids.—**Benzene-disulphonic Acids**, $C_6H_4 \begin{matrix} SO_3H \\ SO_3H \end{matrix}$. On heating benzene with fuming sulphuric acid to 200° C., we get *meta-* and *para* benzene disulphonic acids, with the former in predominating quantity, but by prolonged heating it passes into the *para*-variety (B. 9, 550). *Meta*-disulphonic acid (1,3) is produced from disulphanilic acid (p. 137) by means of the diazo-compound.

Orthobenzene disulphonic acid is formed from meta-amidobenzene sulphonic acid by further introduction of the sulpho-group, and replacement of NH_2 by hydrogen. The melting points of the sulpho-chlorides and sulphamides of the three isomeric disulphonic acids are:

	Ortho.	Meta.	Para.
$C_6H_4(SO_2Cl)_2$	105°	63°	132°
$C_6H_4(SO_2NH_2)_2$	233°	228°	288°.

The corresponding *dicyanides*, $C_6H_4(CN)_2$, the nitriles of the three phthalic acids, are obtained by distillation with potassium cyanide or potassium ferrocyanide. When fused with potassium hydroxide, both *meta* and *para* acids yield resorcinol (metadioxybenzene); at lower temperatures metaphenol sulphonic acid, $C_6H_4(OH)SO_3H$, results at first from both acids.

Benzene-trisulphonic Acid, $C_6H_3(SO_3H)_3$(1,3,6), is easily made by heating potassium m-benzene disulphonate with common sulphuric acid (B. 21, R. 49). The free acid (from the lead salt) crystallizes in long needles with $3H_2O$; its *chloride* melts at 184°, its *amide* at 306°. Fused with caustic potash it yields *phloroglucin*, $C_6H_3(OH)_3$, and upon heating with potassium cyanide it forms the nitrile, which upon saponification becomes *trimesic acid*, $C_6H_3(CO_2H)_3$.

Toluene Disulphonic Acids.—The six possible isomerides are known (B. 20, 350; 29, R. 868). *Xylene Disulphonic Acids* (B. 25, R. 790).

Chlor-, Brom-, Iod-, Iodoso-, Nitro-, Nitroso-, and Amidobenzene Sulphonic Acids.—The chlor-, brom-, and iod-benzene sulphonic acids are prepared from the three amidobenzene sulphonic acids by means of the diazo-reactions (B. 28, 90). p-Compounds are the principal products in the sulphonation of chlor- and brom-benzenes. In nitrating benzene-sulphonic acid and sulphonating nitro-benzene the three isomeric nitro-benzene-sulphonic acids are produced with the m-derivatives in predominating quantity (A. 177, 60).

The following table contains the melting points of the chlorides and amides of the acids:

	Ortho.		Meta.		Para.	
	Chloride.	Amide.	Chloride.	Amide.	Chloride.	Amide.
Chlorsulpho-	28°	188°	Oil	148°	53°	143°
Bromsulpho-	51°	186°	Oil	154°	75°	166°
Iodsulpho-	51°	170°	23°	152°	84°	183°
Nitrosulpho-	67°	186°	60°	161°	Oil	181°

o-*Iod-chloride-benzene sulphochloride*, $ICl_2[2]C_6H_4[1]SO_2Cl$, melting at 60°, is converted by sodium hydroxide into *iodoso-benzene-sulphonic acid* (B. 28, 95).

The compounds resulting from the action of hydriodic acid upon the nitrobenzene-sulpho-chlorides, $C_6H_4(NO_2)SO_2Cl$, and formerly regarded as *sulphimidobenzenes*, $C_6H_4<{NH \atop SO_2}>$, represent *nitrodiphenyldisulphides*, $(C_6H_4 . NO_2)_2S_2$ (B. 21, 1099). m-*Nitrosobenzene-sulphonic Acid* (B. 25, 75).

Amidobenzene-sulphonic Acids.—The three acids are produced by the reduction of the three nitrobenzene sulphonic acids. On sulphonating aniline at 180° with fuming sulphuric acid (8-10 per cent. SO_3), the p-derivative constitutes the chief product. It is *sulphanilic acid*, important in the technology of dyes, and was discovered in 1845 by Gerhardt. The second sulpho-group enters the o-position with the formation of 1-*aniline*-2,4-*disulphonic acid* or *disulphanilic acid;* a trisulphonic acid has not been produced (B. 23, 2143). The amidobenzene-sulphonic acids, like *glycocoll* (1, 354) and *taurine* (1, 306) can be regarded as cyclic ammonium salts: $C_6H_4\begin{matrix} \diagup SO_2O \\ \diagdown NH_3 \end{matrix}$.

The three amido-benzene sulphonic acids dissolve with difficulty in water, alcohol, and ether. The (ortho)-acid either crystallizes in anhydrous rhombohedra or in four-sided prisms containing $\frac{1}{2}H_2O$; these do not effloresce. It is best prepared by the reduction of p-brom-aniline-o-sulphonic acid (B. 28, R. 751; 29, 1075). The (1,3)-acid, called metanilic acid, and also important in the technology of dyes, crystallizes in delicate needles or in prisms with $1\frac{1}{2}H_2O$, which effloresce.

Sulphanilic Acid crystallizes from hot water in rhombic plates with 1 molecule H_2O; these effloresce in the air. They are soluble in 112 parts H_2O at 15° (B 14, 1933). It yields a considerable quantity of quinone when oxidized with MnO_2 and H_2SO_4 or chromic acid. It yields aniline and not amidophenol when fused with caustic potash; unlike its isomerides it is readily converted by bromine water into tribromaniline (B. 29, R. 309).

The sodium amido-benzene-sulphonates yield acetyl derivatives with acetic anhydride (B. 17, 708), whereas the free acids are not in condition to do this. This fact argues for the ammonium salt formula of the three acids.

Diazobenzene-sulphonic Acid Anhydrides, Cyclic Diazides.—Nitrous acid transforms the three amido-benzene-sulphonic acids into the anhydrides of the *diazobenzene-sulphonic acids:*

$C_6H_4<{SO_2OH \atop N_2OH}$	$C_6H_4<{SO_2 \atop N_2}>O$
Diazobenzene-sulphonic Acid	Anhydride.

The hydrated sulpho-acids are not known; they pass at once into anhydrides. The *di-potassium* and the *di-sodium salts* of the o- and p-diazobenzene sulphonic acids, $C_6H_4(SO_3Me)(N_2OMe)$, exist each in two forms, one of which belongs to the normal and the other to the isodiazo-series (p. 101). The *iso-salts* are produced on digesting the normal salts; they give up nitrogen less readily and do not combine, or at least with difficulty, with aromatic amines or phenols, to yield azo-dyes (B. 29, 1059, 1388). *Primary Potassium Isodiazosulphonate*, $C_6H_4(SO_3K)N_2OH + H_2O$, results on treating the corresponding dipotassium salt with acetic acid (B. 28, 1386). A bleaching lime solution oxidizes the diazide of sulphanilic acid to the compound $C_6H_4(SO_3H)N_2O_3H$, which must probably be regarded as an *oxynitramine*, $C_6H_4(SO_3H)N(OH)NO_2$ (B. 29, 2948).

It is rather remarkable that, while otherwise it is only the ortho-compounds of the benzene di-derivatives which form inner anhydrides, *all three of the diazobenzene sulpho-acids are capable of anhydride formation.* They exhibit all of the reactions of the diazo-compounds.

The *diazide of sulphanilic acid*, p-diazobenzene-sulphonic acid, consists of sparingly soluble, white needles; heated with absolute alcohol, it forms benzene-sulphonic acid; with water the diazo-acid becomes p-phenol-sulphonic acid; while with potassium sulphide the di-potassium salt of p-thiophenolsulphonic acid results.

Amido-azo-benzene-sulphonic Acids.—The diazides of sulphanilic acid and metanilic acid are used in the manufacture of *sulphurized azo-dyes:* The first group of

this great class of dyes has received mention (p. 114); it comprises the amido-azo-compounds, which are insoluble or dissolve with difficulty in water. Upon introducing the sulpho-group into the amido-azo-derivatives it will be discovered that the solubility in general increases with the number of sulpho-groups. The alkali salts of the amido-azo-benzene-sulphonic acids constitute the dyes soluble in water. We shall meet with other groups of azo-dyes when we study the phenols: *oxyazo-compounds*. The *naphthalene-azo-compounds* and the *benzidine-dyes*, containing the diphenyl residue, are especially important.

Arbitrary names are assigned these *dyes*, with the addition of the letters Y (yellow), O (orange), and R (red), whose number approximately expresses the intensity of the color. They color wool and silk directly, cotton after it has been mordanted.

Formation.—(1) The amido-azo-bodies are sulphurized. (2) The diazides of sulphonic acids are combined with bases.

Upon sulphonating amido-azobenzene there results a mixture of amido-azobenzene mono- and di-sulphonic acids, known in commerce under the names *acid yellow* or *pure yellow*: $SO_3H[4]C_6H_4[1]N = N[1']C_6H_4[4']NH_2$ and $SO_3H[4]C_6H_4[1]N = N[1']\cdot C_6H_3[4']NH_2[3']SO_3H$ (B. **22**, 847). Being amido-bodies the sulpho-acids are themselves capable again of diazotizing and combination, whereby very valuable dyes have been obtained (compare *Biebrich scarlet*).

The following azo-dyes have been made by combining the diazide of sulphanilic acid with dimethylaniline and diphenylamine, and the diazide of metanilic acid with diphenylamine:

[4']-*Dimethylamido-azo-benzene*-[4]-*sulphonic acid*, $SO_3H[4]C_6H_4[1]N = N[1]C_6H_4[4']N(CH_3)_2$, melting at 112°, consists of golden-yellow leaflets (B. **10**, 528; **12**, 1490). Its sodium salt, as a dye, bears the names *tropæoline* O, *orange* III, and *helianthine*. It serves as a delicate indicator in alkalimetry; mineral acids convert the alkaline orange-colored solution into a rose-red. CO_2, H_2S, and acetic acid do not act on it in the cold (Ch. Z., VI, 1249; B. **18**, 3290). By reduction *helianthine* yields sulphanilic acid and para-amido-dimethyl aniline (p. 95).

[4']-*Phenylamido-azobenzene*-[4]-*sulphonic Acid*, $SO_3H[4]C_6H_4[1]N = N[1]C_6H_4[4']NHC_6H_5$. Its sodium salt dyes wool and silk a beautiful orange, and as a dye is known by the names *tropæoline* OO, *orange* IV. It is used as an indicator in alkalimetry (B. **16**, 1989). By decomposition it yields sulphanilic acid and p-amido-diphenylamine.

[4']-*Phenylamido-azobenzene*-[3]-*sulphonic Acid* is formed from metanilic acid and bears the name *metanil yellow*.

Phenylhydrazine Sulphonic Acids are produced upon reducing the diazides of aniline sulphonic acids with sodium sulphite or stannous chloride (B. **22**, R. 216), and by the direct action of concentrated sulphuric acid upon phenylhydrazines (B. **18**, 3172).

Phenylhydrazine-p-sulphonic Acid, $C_6H_4.(NH.NH_2)SO_3H$, is not readily soluble in water. It is used in the preparation of tartrazine (vol. 1), having the following constitution:

$$\begin{array}{lcl} & & N - NHC_6H_4SO_3Na \\ & & \ \Vert \\ CO_2NaC & - & C - CO \\ \ \ \Vert & & \quad\ \ | \\ \ \ N & \text{———} & NC_6H_4SO_3Na. \end{array}$$

Hydrazobenzene-m-*disulphonic Acid*, $SO_3H[3]C_6H_4[1]NH - NH[1]C_6H_4[3']SO_3H$, has been prepared by the reduction of m-nitrobenzene sulphonic acid, and is converted into benzidine disulphonic acid by hydrochloric acid (B. **21**, R. 323; **23**, 1053).

Sulphinic Acids (compare 1, 153).—*Formation*: (1) By the action of zinc dust upon the ethereal solution of the sulphonic acid chlorides; (2) from the latter and thiophenol salts:

$$C_6H_5SO_2Cl + 2C_6H_5SNa = C_6H_5SO_2Na + NaCl + (C_6H_5S)_2;$$

(3) from SO_2 and benzene in the presence of aluminium chloride (B. **20**, 195); (4) by the action of sodium upon the sulphones (B. **26**, 2813); (5) by the decomposition of the benzene sulph-hydroxamic acids (p. 135).

Deportment.—The *sulphinic acids* are not very stable, and when heated with water, split up into sulphonic acids and *disulphoxides*.

The air and oxidizing agents (especially BaO_2) convert them into sulphonic acids. Their salts unite with sulphur, forming thiosulphonates. When fused with alkalies, they decompose into benzenes and alkaline sulphites.

Benzene sulphinic acid and quinone unite to unsym.-p-*dioxydiphenylsulphone*, $(HO)_2$-$[2,5]C_6H_3[1]SO_2C_6H_5$ (B. **27**, 3259); it also reacts with a number of other substances containing quinoid linkages (compare B. **29**, 2019).

Their alkali salts and alkyl iodides yield mixed sulphones, and with chlorcarbonic esters they form the real sulphinic esters (B. **26**, 308, 430):

$$C_6H_5SO_2Na + ClCO_2C_2H_5 = C_6H_5 . SOOC_2H_5 + NaCl + CO_2.$$

Benzene Sulphinic Acid, $C_6H_5 . SO . OH$, melts at 83°. *Zinc Salt*, $(C_6H_5SO_2)_2$-$Zn + 2H_2O$. *Ethyl Ester*, sp. gr. 1.141 (20°), decomposes when it is heated.

o-*Toluene Sulphinic Acid*, $C_6H_4[1](CH_3)[2]SOOH$, melts at 80° (J. pr. Ch. **54**, 517).

Benzene Thiosulphonic Acid.—Its salts result from the chloride of benzene sulphonic acid and alkali sulphides, as well as from the interaction of benzene sulphinates and sulphur (B. **25**, 1477).

Disulphoxides or Esters of the Thiosulphonic Acids.—*Alkyl* esters and *alkylen esters* of benzene thiosulphonic acid result from the interaction of the potassium salt with the corresponding bromides (B. **25**, 1477).

Phenyl esters—e.g., $C_6H_5 . SO_2 . S . C_6H_5$—are obtained (1) by oxidizing the thiophenols with nitric acid, and (2) by heating the sulphinic acids with water to 130°.

Benzene Disulphoxide, $C_6H_5 . SO_2 . S . C_6H_5$, melting at 45°, is insoluble in water, but dissolves readily in alcohol and ether (B. **20**, 2090).

Sulphobenzene Sulphide, $(C_6H_5SO_2)_2S$, melting at 133°, and **Sulphobenzene Disulphide**, $(C_6H_5SO_2)_2S_2$, melting at 76°, result from the action of iodine and of chlorine upon potassium benzene thiosulphonate (B. **24**, 1141).

Diphenylsulphoxide, *Thionyl Benzene*, $(C_6H_5)_2SO$, melting at 70°, is produced by the action of SO_2 or SO_2Cl_2 upon benzenes in the presence of $AlCl_3$ (B. **20**, 195; **27**, 2547). Potassium permanganate oxidizes it to diphenyl sulphone.

Diphenylselenium Oxide, $(C_6H_5)_2SeO$, has been prepared by oxidizing diphenylselenide (see this), or from the dibromide of the latter (B. **29**, 424).

Sulphones.—The *alkylalphyl sulphones* are isomeric with the esters of the alkyl sulphinic acids. They result from the sodium sulphinates and the alkylogens. The purely *aromatic* sulphones are obtained (1) by the action of SO_3 or chlorsulphonic acid upon benzenes (together with sulphonic acids), $2C_6H_6 + SO_3 = (C_6H_5)_2SO_2 + H_2O$; (2) by the distillation of sulphonic acids (together with benzenes); (3) by the oxidation of the phenyl sulphides; (4) on heating benzene-sulphonic acids with benzenes and P_2O_5; (5) by the action of zinc dust or aluminium chloride upon a mixture of the sulphonic chlorides and benzenes:

$$C_6H_5SO_2Cl + C_6H_5CH_3 \longrightarrow \left.\begin{matrix} C_6H_5 \\ CH_3[1]C_6H_4[4] \end{matrix}\right\} SO_2 \longleftarrow C_6H_6 + CH_3[1]C_6H_4[4]SO_2Cl.$$

The same phenyl p-tolyl-sulphone results from benzene sulphonic acid and toluene as from p toluene-sulphonic acid chloride and benzene, which would prove *that both groups are in union with sulphur* and *that the latter is sexivalent* (B. **11**, 2181); (6) oxy- and amido-substituted sulphones result from the union of sulphinic acids with quinone- and quinone-imide derivatives (B. **29**, 2024).

Phenylethyl Sulphone, $C_6H_5SO_2C_2H_5$, melts at 42° and boils above 300°. *Phenylethyl Sulphone Alcohol*, $C_6H_5 . SO_2 . CH_2 . CH_2OH$, is a syrup formed from ethylene chlorhydrin and sodium benzene sulphinate, as well as by the action of concentrated sodium hydroxide upon *ethylene diphenyl disulphone*, $C_6H_5SO_2 . CH_2 . CH_2 . SO_2 . C_6H_5$, melting at 180°. Phenyl sulphone ethyl alcohol upon oxidation yields *phenyl sulphone acetic acid*, $C_6H_5SO_2CH_2 . CO_2H$, melting at 112°; caustic potash resolves this into CO_2 and *phenyl methyl sulphone*, $C_6H_5 . SO_2 . CH_3$, melting at 88°. The hydrogen of the CH_2-group in the esters of phenyl-sulphone acetic acid is, indeed, replaceable by sodium, but not by alkyls (B. **22**, 1447; **23**, 1647). *Phenyl Allyl Sulphone*, C_6H_5-$SO_2 . C_3H_5$, is an oil (A. **283**, 185).

The α- and β-phenyl-sulphone propionic acids, melting at 115° and 123° (B. **21**, 89), as well as numerous other mixed fatty-aromatic sulphones of the greatest variety, have also been prepared. The phenyl groups have also been replaced by tolyl groups.

Diphenylsulphone, $(C_6H_5)_2SO_2$, *Benzene Sulphone, Sulphobenzide*, melting at 128° and boiling at 276°, is formed by the distillation of benzene sulphonic acid, and by the oxidation of phenyl sulphide, $(C_6H_5)_2S$, and *diphenylsulphoxide* (see above); further, from benzene sulphonic chloride, $C_6H_5 . SO_2Cl$, and mercury diphenyl, as well as from benzene and benzene sulphonic chloride or sulphuryl chloride with aluminium chloride (B. **26**, 2940). It is also obtained by the action of fuming sulphuric acid or SO_3 upon benzene. It is converted into benzene-sulphonic acid when digested with concentrated sulphuric acid. When heated with PCl_5, or in a current of chlorine gas, it is decomposed into chlorbenzene and the chloride of benzene sulphonic acid.

With sulphur or selenium it forms the diphenylsulphone: *Diphenylsulphide* or *diphenylselenide* (B. **27**, 1761). Sodium converts it into sodium benzene sulphinate and diphenyl (B. **26**, 2813). *Diphenyl Selenone*, $(C_6H_5)_2SeO_2$, melting at 155° and boiling at 271°, results on oxidizing diphenyl selenium oxide with potassium permanganate (B. **29**, 424).

7. PHENOLS.

The phenols are derived from the aromatic hydrocarbons by the replacement of hydrogen of the benzene residue by hydroxyl. The phenols, like the alcohols, are distinguished as mono-, di-, and trihydric, according to the number of hydroxyl groups which have entered. All of the six hydrogen atoms in benzene can be substituted by hydroxyl groups. The phenols correspond to the tertiary alcohols, as they yield neither acids nor ketones upon oxidation. Their acid nature, distinguishing them from alcohols, is governed by the more negative nature of the phenyl group, and is enhanced by the entrance of more negative groups (see picric acid, p. 150). In contrast to the phenols the aromatic alcohols, which are their isomerides, and have hydrogen of the side-chains replaced by hydroxyl, approach the aliphatic alcohols in their deportment.

Various representatives of the phenols have been found in the vegetable kingdom.

Some of them occur already formed as phenol-sulphonic acids in the urine of mammalia. In the organism of the latter many organic bodies are oxidized to phenols: benzene to phenol, brombenzene to bromphenol, aniline to amidophenol, phenol to hydroquinone. In the decay of albumin the presence of phenols has also been established.

Phenols are produced in the dry distillation of wood, particularly beech-wood, turf, bituminous coal (B. **26**, R. 151), and anthracite coal.

To isolate the phenols from coal tar shake the latter with caustic alkali in which they are soluble. Acids liberate them from this solution, and then they can be purified by fractional distillation.

MONOHYDRIC PHENOLS.

In addition to the methods of formation just given, the following are worthy of note:

(1) The decomposition of the diazo-derivatives, especially their sulphates, with boiling water (p. 105).

(2) Fusion of the sulphonic acids with potassium or sodium hydroxide. This reaction was discovered in 1867 by Kekulé, Würtz, and Dusart, independently of each other:

$$C_6H_5 . SO_3K + KOH = C_6H_5 . OH + SO_3K_2.$$

In practice this method is used to obtain phenols from sulphoacids, the operation being carried out in iron vessels.

The experiment in the laboratory is executed in a silver or nickel dish, the fusion supersaturated with sulphuric acid, and the phenol extracted by shaking with ether.

In fusing sulphonic acids or phenols containing halogens, the latter are also replaced with formation of polyhydric phenols. Occasionally the sulpho-group splits off as sulphate and is replaced by hydrogen; thus, cresolsulphonic acid yields cresol.

(3) The halogen benzene substitution products do not react with alkalies; but if nitro-groups are present at the same time, the halogens are replaced even by digesting with aqueous alkalies—this will occur the more readily if the nitro-groups be multiplied. In this respect they approach the acid chlorides:

$$\underset{\text{Picryl Chloride}}{C_6H_2(NO_2)_3Cl} + H_2O = \underset{\text{Picric Acid.}}{C_6H_2(NO_2)_3OH} + HCl$$

(4) The amide-group in the nitroamido-derivatives can also be replaced by hydroxyl on boiling with aqueous alkalies; ortho- and para-nitranilines, $C_6H_4(NO_2) . NH_2$ (not meta), yield their corresponding nitrophenols. The ortho-dinitro-products react similarly (p. 67).

(5) Small quantities of phenol can be obtained from benzene by the action of ozone, hydrogen peroxide (palladium hydride and water), and by shaking with sodium hydroxide and air (B. 14, 1144). By the addition of oxygen to benzene through the instrumentality of aluminium chloride.

(6) By the *breaking down* of phenol carboxylic acids, when their salts are subjected to dry distillation with lime.

(7) The *synthesis* of the higher phenols by introduction of alkyls into the benzene nucleus takes place readily on heating the phenols with alcohols and $ZnCl_2$ to 200° (B. 14, 1842; 17, 669; 27, 1614; 28, 407):

$$C_6H_5 . OH + (CH_3)_2CH . CH_2 . OH = (CH_3)_2CH[4]C_6H_4[1]OH.$$

Alkyl ethers of the phenols are simultaneously produced; methyl alcohol yields methyl-phenol $C_6H_5 . O . CH_3$. Magnesium chloride (B. 16, 792) and primary alkali sulphates (B. 16, 2541) possess the same condensing power as $ZnCl_2$.

(8) Phenols, under the influence of concentrated sulphuric acid, take up unsaturated hydrocarbons—*e. g.*, isoamylene—and form alkyl phenols (B. 25, 2649).

Deportment: Replacement of the Hydrogen Atoms.—(1) The character of the phenols, recalling the acids, expresses itself in the ease with which they form salts, particularly with the alkalies. The hydrogen of the hydroxyl group is also readily replaced (2) by alcohol radicals and (3) by acid radicals. (4) The presence of an hydroxyl group in the place of an aromatic hydrogen atom renders more easy the substitution of other hydrogen atoms by chlorine, bromine, and the nitro-group.

(5) The phenols unite with the diazo-compounds, forming azo- and diazo-dyes: oxy-azo-derivatives (p. 155).

(6) *Color Reactions of the Phenols.*—On adding phenols (mono- or polyhydric) to a solution of KNO_2 (6 per cent.) in concentrated sulphuric acid, intense colorations arise; with common phenol we get first a brown, then green, and finally a royal-blue color (Reaction of Liebermann) (see B. 17, 1875). Dyes are produced in this manner; their character is as yet unexplained. They have been called **dichroïnes** (B. 21, 249).

The phenols afford similar colors in the presence of sulphuric acid, with diazo-compounds, and nitroso-derivatives. Ferric chloride imparts color to the solutions of most phenols. Mercury nitrate, containing nitrous acid, colors nearly all the phenols red (reaction of Plugge) (B. 23, R. 202).

Replacement of the Hydroxyl Group.—(7) When heated with zinc dust the phenols are reduced to hydrocarbons.

(8) The oxygen of the simple phenols is not very easily replaced by chlorine when phosphorus pentachloride acts upon them. Phenol itself has given the body, $C_6H_5OPCl_4$ (p. 147). The pentachloride acts with greater ease upon the nitrophenols, forming nitro-chlorbenzenes.

(9) Phosphorus sulphide converts the phenols into thio-phenols.

(10*a*) The anilines result on heating with zinc ammonium chloride (compare p. 72).

(10*b*) In the alcohol-ethers of the nitro phenols (as with the acid esters) we can replace the OH by NH_2, on heating with alcoholic ammonia.

(11) For the oxidation of the alkyl residues of homologous phenols see p. 143.

Nucleus-syntheses.—(1) Compare methods 7 and 8 (p. 141), upon the replacement of the aromatic hydrogen atoms of the phenols by alkyl groups.

(2) The alkali salts of the phenols are converted by carbon dioxide, at higher temperatures, into the alkali salts of oxy-acids—*phenol carboxylic acids* (compare salicylic acid).

(3) The phenols also yield *phenol carboxylic acids* with carbon tetrachloride and sodium hydroxide.

(4) Oxyaldehydes or phenol aldehydes (see salicylaldehyde) are produced from phenols, chloroform (1, 235), and caustic soda.

(5) The phenols condense with formaldehyde to *phenol alcohols* (see saligenine). (6) *Coumarines* (see these) are formed on heating phenols with malic acid and sulphuric acid. (7) Dyestuffs belonging to the *aurine* series, and derived from triphenylmethane, $CH(C_6H_5)_3$ (see this), are obtained from the phenols by their action upon benzotrichloride, $C_6H_5 . CCl_3$. (8) The so-called *phthaleins* are combinations of phthalic acid and o-sulphobenzoic anhydride with the phenols.

Breaking-down of the Benzene Nucleus of the Phenols (pp. 44, 45).

(1) By oxidation of phenol (see this).

(2) By treating the phenols with chlorine, and then decomposing the chlorine addition products with alkalies.

Benzophenol, Phenol, *Carbolic Acid,* $C_6H_5 . OH$, melts at 43° and boils at 183°; its specific gravity is 1.084 (0°). It is obtained from amidobenzene, from benzene-sulphonic acid, from the three oxy-benzoic acids, etc., by the methods previously described. It occurs already formed in *Castoreum* and in the urine of the herbivoræ.

Commercial phenol is a colorless, crystalline mass, which gradually acquires a reddish color on exposure to the air (B. 27, R. 790). Pure phenol crystallizes in long, colorless prisms. It possesses a characteristic odor, burning taste, and poisonous and antiseptic properties. It dissolves in 15 parts water at 20°, and very readily in alcohol, ether, and glacial acetic acid. It is volatile with steam. Ferric salts impart a violet color to its neutral solutions. Bromine water precipitates [2,4,6]-tribromphenol from even very dilute solutions.

Diphenols, $C_{12}H_8(OH)_2$, derivatives of diphenyl (see this), are produced on fusing phenol with caustic potash.

Diphenylene oxide is produced when phenol is distilled over lead oxide. *Aurine* results when it is heated with oxalic or formic acid and dehydrating agents (see this). Potassium permanganate oxidizes phenol to inactive or mesotartaric acid (vol. 1). Chlorine finally changes phenol to keto-chlorides, which are derived from di- and tetrahydrobenzene (B. **27**, 537). Chlorine and caustic soda convert phenol into trichlor-R-pentene dioxycarboxylic acid (p. 27). The most important reactions of phenol have been previously described.

History.—Runge discovered (1834) phenol in coal tar and called it carbon oil acid, or carbolic acid. He also observed the physiological properties it possessed in common with creosote. Laurent, in 1841, first obtained it pure and gave it the names *hydrate de phènyle* or *acide phènique*, from φαίνειν, to illuminate, probably because it occurs in the tar produced in the manufacture of illuminating gas. Gerhardt, who prepared it from salicylic acid, introduced the name phenol, indicating thereby that it was an alcohol. In 1867 Lister, of Glasgow, showed its great importance in surgery as a disinfectant.

Phenolates.—*Phenates, Potassium Phenate*, C_6H_5OK, and *Sodium Phenate*, C_6H_5ONa, are obtained by dissolving phenol in caustic potash or soda, evaporating the solution and sharply drying the residue. Both salts dissolve readily in water (B. **26**, R. 150). Carbon dioxide sets phenol free from them; it is, therefore, not soluble in the alkali carbonates.

Calcium Phenate, $(C_6H_5O)_2Ca$, and *Mercury Phenate*, $(C_6H_5O)_2Hg$. (See B. **29**, R. 178, for the compounds of the phenols with aluminium chloride.)

Homologous Phenols.—It is strange that the *cresols*, as well as other higher phenols, can not be oxidized by the chromic acid mixture; *the OH-group prevents the oxidation of the alkyl groups by chromic acid.* If, however, the phenol hydrogen is replaced by alkyls or acid radicals (in the phenol ethers and esters), then the oxidation of the alkyl does take place with the production of ether acids or ester acids.

The readily prepared sulphuric or phosphoric acid esters of the homologous phenols are best adapted for oxidation with an alkaline permanganate solution (B. **19**, 3304), whereas the free phenols are completely destroyed by this reagent (compare oxidation of phenol, above).

The oxidation of the alkyls in the sulpho-acids of the homologous phenols is similarly influenced by the sulpho-group. In general *negative atoms or groups prevent the oxidation of alkyls in the ortho-position by acid oxidants*, whereas alkaline oxidants—*e. g.*, $KMnO_4$—do precisely the reverse in that they first oxidize the alkyl group holding the ortho-position (A. **220**, 16). The methyl groups of the methyl phenols, such as the cresols and xylenols, are converted by molten alkalies into carboxyl groups, and there result oxybenzoic acids, oxytoluic acids, oxyphthalic acids, etc. (compare the like behavior of the homologous *pyrrols* and *indols*).

Other rearrangement reactions are given on p. 142. The liquid homologous phenols are particularly characterized by the melting points of their benzoyl esters; therefore these will be given in connection with the various members.

1. **Cresols, Oxytoluenes**, $CH_3 . C_6H_4OH$.—The three isomerides occur in coal-tar and beech-wood tar.

They are obtained from the toluidines by method 1, and from the toluene-sulphonic acids by method 2 (p. 141). They have a similar odor, but it is more disagreeable than that of phenol. They are less poisonous, and are disinfectants. They are changed to toluene when heated with zinc dust. Sodium and carbon dioxide produce the corresponding cresotinic acids.

See above for their behavior toward molten caustic potash and other oxidizing

agents. o-Cresol is obtained from carvacrol (p. 145) and the m-body from thymol (see below). The latter is also prepared from the dibromide of synthetic β-methylketo-R-hexene (see this) by the elimination of hydrogen bromide (A. **281**, 98).

o-Cresol, [1,2]-*Oxytoluene*,	melts at 31°	and boils at	188°.
m-Cresol, [1,3]-*Oxytoluene*,	" 4°	"	201°.
p-Cresol, [1,4]-*Oxytoluene*,	" 36°	"	198°.

Ferric chloride colors o-cresol blue. The crude cresols are used as disinfectants: *creolin* is a solution of the crude cresols in alkalies; *cresolin* is a solution of the same in resin soaps, while *lysene* or *lysol* is a solution of crude cresols in olive soaps. See B. **14**, 687, for the behavior of the cresols in the animal organism.

2. **Phenols**, C_8H_9OH.—Oxydimethyl benzenes and oxyethyl benzenes. The six possible *xylenols*, $C_6H_3(CH_3)_2 . OH$, have been prepared.

Ethyl Phenols, $C_6H_4(C_2H_5) . OH$.—From the ethyl-benzene-sulphonic acids (B. **27**, R. 189). The *ortho*-compound is a liquid, boiling at 203°; its benzoyl derivative melts at 39°. The *meta* boils at 214°; its benzoyl derivative melts at 52°. The *para* is a solid, melts at 45°, and boils at 215°; its benzoyl compound melts at 59°.

3. **Phenols**, $C_9H_{11} . OH$.—*Mesitol*, $C_6H_2(CH_3)_3 . OH$, from amido-mesitylene and mesitylene-sulphonic acid, melts at 68° and boils at 220°. [1]OH[2,4,5]-*Pseudocumenol*, $C_6H_2(CH_3)_3 . OH$, from pseudocumene-sulphonic acid, melts at 73° and boils at 232° (B. **17**, 2976).

m-n-*Propyl Phenol*, from isosafrol, melts at 26° and boils at 228° (B. **23**, 1162). p-n-*Propyl Phenol* boils at 232°. p-*Isopropyl Phenol* melts at 61° and boils at 229°. It is also produced along with hydroquinone (p. 162) on decomposing diphenol-β-propane, $(CH_3)_2C(C_6H_4OH)_2$ (from the action of fuming hydrochloric acid on acetone and phenol), with molten caustic potash (B. **25**, R. 334).

4. **Phenols**, $C_{10}H_{13} . OH$.—There are twenty possible isomerides. Thymol and carvacrol merit notice. They occur in vegetable oils. Both are derivatives of ordinary p-cymene (p. 56), and contain the isopropyl group.

Thymol, when heated with P_2O_5, breaks down into propylene and m-cresol, while carvacrol, under similar treatment, yields propylene and o-cresol.

Thymol, = [3]-Methyl-[6]-isopropyl phenol, $C_3H_7[6]C_6H_3\begin{cases}[1]OH\\[3]CH_3\end{cases}$

Carvacrol, = [2]-Methyl-[5]-isopropyl phenol, $C_3H_7[5]C_6H_3\begin{cases}[1]OH\\[2]CH_3\end{cases}$

Thymol, melting at 44° and boiling at 230°, crystallizes in large, colorless plates. It exists with cymene, $C_{10}H_{14}$, and thymene, $C_{10}H_{16}$, in oil of thyme (from *Thymus vulgaris*), and in the oils of *Ptychotis ajowan* and *Monarda punctata*. To obtain the thymol shake these oils with potassium hydroxide, and from the filtered solution precipitate thymol with hydrochloric acid. It is artificially prepared from nitrocuminaldehyde (see this), as well as from dibrom-menthone, by the splitting-off of hydrogen bromide (B. **29**, 420). It has a thyme-like odor and answers as an antiseptic.

Ordinary cymene is obtained by distilling it with P_2S_5. Thymoquinone (see this) is produced in its oxidation.

Iodine and caustic potash convert thymol into *di-iodthymol*, a diphenyl derivative which has been substituted for iodoform under the names ***aristol*** and ***annidalin***. Compare: Die Arzneimittel der organischen Chemie von Thoms.

Carvacrol, Cymophenol, melting at 0° and boiling at 236°, isomeric with thymol, occurs already formed in the oil of certain varieties of satureja, also in *Briganum hirtum*, and is obtained from an isomeric *carvol*, a dihydrocymene derivative (see this) contained in the oil of *Carvum carvi*, and certain other oils, when it is heated with glacial phosphoric acid (B. **19**, 12). It is further prepared by heating with iodine ($\frac{1}{8}$ part), using a return condenser. It is made artificially from cymene-sulphonic acid (B. **11**, 1060).

Distilled with P_2S_5 it yields cymene and **thiocymene**, *cymothiophenol*, $C_{10}H_{13}.SH$, boiling at 235°.

s-**Carvacrol**, $(CH_3)[3](CH_3)_2CH[5]C_6H_3[1]OH$, melts at 54° and boils at 241° (B. **27**, 2347). *Methyl*-p-norm.-*propyl phenol*, $(CH_3)[2]C_3H_7[5]C_6H_3OH$, from the corresponding sulpho-acid, boils at 240° (B. **29**. R. 417).

p-*Tertiary Butyl Phenol*, $(CH_3)_3C[4]C_6H_4[1]OH$, melting at 98° and boiling at 237°, is obtained from isobutyl alcohol, phenol, and zinc chloride (B. **24**, 2974).

p-*Tertiary Amyl Phenol*, $(CH_3)_2(C_2H_5)C[4]C_6H_4[1]OH$, melting at 93° and boiling at 266°, results from the action of $ZnCl_2$ upon isoamyl alcohol or tertiary amyl alcohol, and from isoamylene, phenol, acetic acid, and sulphuric acid (B. **28**, 407).

Diethyl Phenols (B. **22**, 317).

Tetramethyl Phenols (B. **15**, 1854; **17**, 1916; **18**, 2842; **21**, 645, 907).

Pentamethyl Phenol melts at 125° and boils at 267° (B. **18**, 1826).

DERIVATIVES OF THE MONOHYDRIC PHENOLS.

The behavior of the phenols was given under the example selected—ordinary phenol. Because this can be obtained with comparative ease, more derivatives of it, than of its homologues, have been prepared. In the following pages the derivatives of the homologues will only be brought forward and discussed in case they possess theoretical or practical value, and then in connection with the compounds of the corresponding phenol.

Phenol Alcohol-ethers.—(1) Like the ethers of the aliphatic alcohols (1, 132), they result from the interaction of alkyl iodides and phenates. The phenol is digested with caustic potash and the alkyl iodide or methyl chloride is conducted over sodium phenate heated to 200° (B. **16**, 2513).

(2) By heating a mixture of the alkali salts of the phenols with an excess of alky sulphates, in aqueous or alcoholic solution (B. **19**, R. 139).

(3) Upon heating the benzene-sulphonic esters with phenols (B. **27**, R. 955).

(4) Together with hydrocarbons on decomposing benzene diazo-compounds with alcohols (B. **25**, 1973) (p. 104).

(5) By the dry distillation of the phenol ethers of the oxy-acids with lime or baryta:

$$\underset{\text{Anisic Acid}}{CO_2H[1].C_6H_4[4]OCH_3} \xrightarrow{-CO_2} \underset{\text{Anisol.}}{C_6H_5OCH_3}$$

(6) The phenols are converted at the ordinary temperature by diazomethane, with evolution of nitrogen, into their methyl ethers (B. **28**, 857):

$$C_6H_5OH + CH_2N_2 = C_6H_5OCH_3 + N_2.$$

Boiling alkalies do not alter the alcohol ethers. When, however, they are heated with hydriodic or hydrochloric acid, they split up into their components:

$$C_6H_5 . O . CH_3 + HI = C_6H_5 . OH + CH_3I.$$

Al_2Cl_6 also decomposes them (B. **25**, 3531). They behave like the aromatic hydrocarbons with Cl, Br, I, NO_3H, and SO_4H_2.

Anisol, Methyl Phenyl Ether, $C_6H_5 . O . CH_3$, is produced by distilling anisic or p-methyl salicylic acid. It boils at 152°; its specific gravity at 15° is 0.991. It is not reduced by zinc dust.

Phenetol, Ethyl Phenyl Ether, $(C_6H_5) . O . C_2H_5$, boils at 172°, and has the specific gravity 0.9822 (0°). The *isoamyl ether* boils at 225°.

Bromethyl Phenyl Ether, $BrCH_2 . CH_2 . O . C_6H_5$, melts at 39° (J. pr. Ch. [2] **24**, 242).

Phenol-ethylene Ether, Glycol-diphenyl Ether, $C_6H_5OCH_2 . CH_2OC_6H_5$, melts at 95°. *Glycol-monophenyl Ether* boils at 165° (80 mm.) (B. **29**, R. 289). *Phenyl Glycerol Ether* (B. **24**, 2146).

Phenoxalkylamines (1, 311).—*β-Phenoxethylamine,* $NH_2 . CH_2 . CH_2 . O . C_6H_5$, boils at 228° (B. **24**, 189). *γ-Phenoxypropylamine,* $NH_2 . CH_2 . CH_2 . CH_2 . O . C_6H_5$, boils at 241° (B. **24**, 2637). [*δ-Amidobutylphenyl Ether*] $NH_2CH_2CH_2 . CH_2 . CH_2OC_6H_5$, boils at 225° (B. **24**, 3232).

Phenol ethers of aldehyde alcohols, ketone alcohols, and alcohol acids have been obtained from the corresponding chlorinated aldehydes, ketones, and carboxylic acids by the action of sodium phenate:

Phenoxyacetaldehyde, $C_6H_5O . CH_2 . CHO$, boils at 119° (30 mm.) (B. **28**, R. 295).

Phenoxyacetone, Phenacetol, $C_6H_5O . CH_2 . CO . CH_3$, boiling at 230°, is condensed by concentrated sulphuric acid to *methyl cumarone* (see this) (B. **28**, 1253). *Phenoxyacetic Acid,* $C_6H_5O . CH_2 . COOH$, melting at 96°, is isomeric with mandelic acid, $C_6H_5CH(OH) . COOH$. It results from monochloracetic acid and potassium phenate at 150°, as well as by the oxidation of phenoxyacetaldehyde. It is a strong antiseptic (B. **19**, 1296; **27**, 2796). *Diphenoxyacetic Acid,* $(C_6H_5O)_2CHCO_2H$, melts at 91° (B. **27**, 2796). *α-* and *γ-Phenoxybutyric Acid* melt at 99° and 60° (B. **29**, 1421). *α-Phenoxyacetoacetic Ester,* $CH_3 . CO . CH(OC_6H_5)CO_2C_2H_5$, from sodium phenate and α-chloracetoacetic ester, is a thick oil. Concentrated sulphuric acid condenses it to *methyl cumarilic ester.*

Phenol Ethers.—Phenyl Ether, $(C_6H_5)_2O$, **Diphenyl Oxide,** melting at 28° and boiling at 252°, is produced by distilling copper benzoate (together with benzoic phenyl ether) and digesting diazobenzene sulphate with phenol (B. **25**, 1973); also by heating phenol with zinc chloride to 350°, or, better, with aluminium chloride (B. **14**, 189). It crystallizes in long needles, and possesses an odor resembling that of geraniums. It dissolves readily in alcohol and ether. It is not reduced on heating with zinc dust or hydriodic acid.

Nitrated phenyl ethers have been obtained by the interaction of the corresponding nitrohaloid benzenes and the potassium salts of phenols: o-*Nitrophenyl Ether,* $C_6H_5O . C_6H_4NO_2$, boils at 235° (60 mm.). o, o'-*Dinitrophenol Ether,* $(NO_2 . C_6H_4)_2O$, melts at 114° (B. **29**, 1880, 2084).

Acid Esters of Phenol.—The *acid esters* are obtained by acting with acid chlorides or anhydrides upon the phenols or their salts; also by digesting the phenols with acids and $POCl_3$. To effect the substitution of all the hydroxyl-hydrogen atoms in the polyhydric phenols by acetyl groups, it is recommended to heat them with acetic anhydride and sodium acetate. On boiling with alkalies, or even with water, they, like all esters, break down into their components.

Esters of Inorganic Acids.—Phenyl Sulphonic Ester is not known in

a free state. Its *sodium salt*, $NaSO_2OC_6H_5$, results from the action of SO_2 upon sodium phenate. Methyl iodide converts it into *methyl sulphonic phenyl ester*, $CH_3SO_2OC_6H_5$ (compare B. **25**, 1875).

Phenylsulphuric Acid, $C_6H_5 . O . SO_3H$, is not known in a free state; when liberated from its salts by concentrated hydrochloric acid, it immediately breaks down into phenol and sulphuric acid. Its *potassium salt*, $C_6H_5 . O . SO_3K$, forms leaflets, not very soluble in cold water, and occurs in the urine of herbivorous animals, and also in that of man and the dog after the ingestion of phenol. It is synthetically prepared, like other phenols, on heating potassium phenoxide with an aqueous solution of potassium pyrosulphate (Baumann, **9**, 1715).

The phenyl sulphuric acids are very stable in aqueous and alkaline solution; upon digesting with mineral acids, however, they are very rapidly decomposed. When potassium phenylsulphate is heated in a tube, it passes quietly into potassium p-phenol-sulphonate.

Phenyl Esters of the Phosphoric Acids.—These arise in the action of PCl_3 and $POCl_3$ (A. **239**, 310; **253**, 120):

Phenylphosphorous Chloride, ...	$C_6H_5O . PCl_2$,	boils at 90° (11 mm.)
Diphenylphosphorous Chloride, ...	$(C_6H_5O)_2PCl$,	" 172° "
Triphenylphosphite, ...	$(C_6H_5O)_3P$,	" 220° "
Phenylphosphoric Chloride, ...	$(C_6H_5O)POCl_2$,	" 121° "
Diphenylphosphoric Chloride, ...	$(C_6H_5O)_2POCl$,	" 195° (14 mm.)
Triphenylphosphate, m. p. 45°, ...	$(C_6H_5O)_3PO$,	" 245° (11 mm.)

(B. **18**, 1700).

The two phenylphosphorous chlorides take up chlorine:

Phenylphosphoric Tetrachloride, ...	$C_6H_5OPCl_4$
Diphenylphosphoric Trichloride, ...	$(C_6H_5O)_2PCl_3$

Phenyl Silicates (B. **18**, 1679).

Phenyl Esters of Monocarboxylic Acids.—*Phenyl Formate* (J. pr. Ch. [2] **31**, 467). *Phenyl-ortho-formic-ester*, $CH(O . C_6H_5)_3$, is formed by boiling phenol with sodium hydroxide and chloroform. It melts at 71° and distils at 265°, under 50 mm. pressure (B. **18**, 2656).

Phenyl Acetate, $CH_3 . COOC_6H_5$, boils at 195° (B. **18**, 1716). *Orthoacetic Phenyl Ester*, $CH_3C(OC_6H_5)_3$, melts at 98° (B. **24**, 3678).

Phenyl Carbonates.—The free phenyl-carbonic acid is not known. The opposite is true of *Sodium Phenyl Carbonate*, $C_6H_5OCO_2Na$. It is produced when CO_2 acts upon sodium phenoxide (under pressure).

It is a white hygroscopic powder, decomposed again by water. When heated under pressure to 120–130°, *sodium salicylate*, $HOC_6H_4CO_2Na$, results, just as phenolsulphonic acid is obtained from phenylsulphuric acid (see above). When heated to 190° with sodium phenate, sodium phenyl carbonate yields *disodium salicylate* and phenol.

Phenyl Carbonate.—The carbonic acid ester, $CO(O . C_6H_5)_2$, is produced on heating phenol and phosgene gas, $COCl_2$, to 150°. It is readily obtained by leading phosgene gas into the aqueous solution of sodium phenylate (J. pr. Ch. **17**, 139; B. **17**, 287). It crystallizes from alcohol in shining needles, and melts at 78°. It yields *sodium salicylate* (see this) when heated to 200° with sodium hydroxide. Urea results if it be heated with ammonia (B. **23**, 694).

Mixed carbonates containing phenol and alkyls—*e. g.*, *phenyl-ethyl carbonate*, $CO_3(C_2H_5)(C_6H_5)$—are produced by the action of chlorformic esters upon the sodium salts of the phenols.

Diphenylthiocarbonic Ester, $C_6H_5OCSOC_6H_5$ (B. **27**, 3410). *Phenyl Carbaminate*, $NH_2COOC_6H_5$, melts at 141° (A. **244**, 43). *Phenylcarbamic Phenyl Ester*, $C_6H_5NHCO_2C_6H_5$, from carbanile (p. 89) and phenol, melts at 124° (B. **18**, 875; **27**, 1370).

Phenylthiocarbamic Phenyl Ester, $C_6H_5O.CSNHC_6H_5$, melting at 148°, is produced on heating phenyl mustard oil with phenol to 280° (B. **29**, R. 177). *Phenylimidocarbonic Phenyl Ester*, $C_6H_5N:C(OC_6H_5)_2$, melting at 136°, is obtained from isocyanphenyl chloride (p. 89) and sodium phenate (B. **28**, 977).

Phenyl-allophanic Ester, $CO<\begin{matrix}NH_2\\NH.CO_2.C_6H_5\end{matrix}$, is produced by conducting cyanic acid vapors into anhydrous phenol. A crystalline mass.

Phenyl Esters of Dicarboxylic Acids.—*Phenyl Oxalic Ester*, $(COOC_6H_5)_2$, melts with decomposition at 130° (J. pr. Ch. [2] **25**, 282). *Ethyl Phenyl Oxalic Ester*, $COOC_2H_5.COOC_6H_5$, boiling at 236°, is obtained from ethyl oxalic chloride (vol. 1). The *succinic ester* melts at 118° and boils at 330°. *Phenyl Fumaric Ester*, melting at 161°, decomposes when distilled slowly into CO_2, phenyl cinnamic ester (see this) and stilbene (see this) (B. **18**, 1948).

PHENOL SUBSTITUTION PRODUCTS.

Phenol Haloids.—*Formation.* (1) Chlorine and bromine react readily with phenols; this is exemplified in bromine precipitating phenol quantitatively from its aqueous solutions as [1OH,2,4,6]-tribromphenol. Chlorine and bromine enter the ortho- and para-positions; there result at first the [1,2]- and [1,4]-mono-, then the [1,2,4]-di-, and finally the [1,2,4,6]-trisubstitution products. At 150–180°, by action of chlorine or bromine vapors, abundant quantities of o-chlor- and o-bromphenol (B. **27**, R. 957) are produced.

The iod-derivatives are formed by adding iodine and iodic acid to a dilute potassium hydroxide solution of phenol:

$$5C_6H_5OH + 2I_2 + IO_3H = 5C_6H_4IOH + 3H_2O,$$

or by the action of iodine and mercuric oxide. Di-iod-phenol is the chief production in the latter case.

(2) From substituted anilines by the replacement of NH_2 by OH, which may be brought about by the diazo-compounds; this reaction leads to pure mono-haloid phenols. (3) From the nitrophenols by replacing the nitro-group with halogens (effected through the amido- and diazo-derivatives). (4) By distilling substituted oxyacids with lime or baryta.

Deportment.—(1) The introduction of halogen atoms considerably increases the acid character of phenol; thus, trichlorphenol readily decomposes the alkaline carbonates. (2) When fused with potassium hydroxide, the halogen is replaced by the hydroxyl group (p. 141).

In this reaction it frequently occurs, especially at high temperatures, that not the corresponding isomerides, but rather the more stable derivative results; for example, all the bromphenols yield resorcinol. The caustic potash fusion is, therefore, not applicable in determining constitution.

(3) Sodium amalgam causes the replacement of the halogen atoms by hydrogen.

Monohaloid Phenols.—The monochlorphenols in particular are characterized by a disagreeable, very adherent odor. The brom- and iod-phenols being attacked at a lower temperature than the chlor-derivatives, are changed on fusing with potash into the corresponding dioxybenzenes. The higher the temperature rises in the fusion of the o- and p-compounds, the greater will be the yield of resorcinol or m-dioxybenzene; the three isomeric monochlorphenols yield resorcinol:

	Ortho-		Meta-		Para-		
	M. P.	B. P.	M. P.	B. P.	M. P.	B. P.	
Chlorphenol,	7°	176°	28°	212°	41°	217°	
Bromphenol,	liquid	195°	32°	236°	66°	238°	
Iodphenol,	43°	—	40°	—	94°	—	(B. **20**, 3019).

See B. **29**, 997, 1409, 2595, for the iodanisols and phenetols.

Polyhaloid Phenols.—In the direct substitution the [2,4]-di- and [2,4,6,]-trihaloids are produced quite readily:

	M. P.	B. P.		M. P.	B. P.
[2,4]-Dichlorphenol,	43°	210°	[2,4,6]-Trichlorphenol,	68°	244°
[2,4]-Dibromphenol,	40°	—	[2,4,6]-Tribromphenol,	92°	—
[2,4]-Di-iodphenol,	72°	—	[2,4,6]-Tri-iodphenol,	156°	—

	M. P.		M. P.
[2,3,4,6]-Tetrachlorphenol,	65° (B. **27**, 549).	Pentachlorphenol,	186° (B. **28**, R. 150).
[2,3,4,6]-Tetrabromphenol,	120° (A. **137**, 209).	Pentabromphenol,	225°.

The tri-, tetra-, and penta-chlor- and -bromphenols take up chlorine and bromine, becoming chlorinated and brominated *oxodi-* and *oxotetrahydrobenzenes* (see also B. **28**, R. 1012). 2,4,5-Pseudocumenol yields, when brominated under suitable conditions, a *tribrompseudo-cumenol*, insoluble in alkali. It is distinguished by the great reactivity of one of its bromine atoms. Its peculiar behavior renders it very probable that it is really a derivative of *keto-dihydrobenzene* (B. **29**, 2329; **30**, 744, 753). 2,5-*Xylenol* yields a very similar tribrom-derivative (B. **29**, 2348).

NITROPHENOLS.

The phenols, like the anilines, are very readily nitrated. The entrance of the nitro-groups increases their acid character very considerably. All nitrophenols decompose alkaline carbonates. Trinitrophenol is a perfect acid in its behavior; its chloranhydride, $C_6H_2(NO_2)_3Cl$, reacts quite readily with water, re-forming trinitrophenol (p. 68). The benzene nucleus of the nitrophenols is capable of ready substitution with the halogens; whereas the nitrohydrocarbons are chlorinated with difficulty.

The nitro-groups replace the o- and p-hydrogen atoms referred to hydroxyl, and with reference to one another in the m-position:

$$C_6H_5OH \left\{ \begin{array}{l} \longrightarrow C_6H_4 \left\{ \begin{array}{l} [1]OH \\ [2]NO_2 \end{array} \right. \longrightarrow C_6H_3 \left\{ \begin{array}{l} [1]OH \\ [2]NO_2 \\ [6]NO_2 \end{array} \right. \\ \longrightarrow C_6H_4 \left\{ \begin{array}{l} [1]OH \\ [4]NO_2 \end{array} \right. \longrightarrow C_6H_3 \left\{ \begin{array}{l} [1]OH \\ [2]NO_2 \\ [4]NO_2 \end{array} \right. \end{array} \right\} \longrightarrow C_6H_2 \left\{ \begin{array}{l} [1]OH \\ [2]NO_2 \\ [4]NO_2 \\ [6]NO_2 \end{array} \right.$$

Mononitrophenols, $NO_2 . C_6H_4 . OH$.—Dilute nitric acid converts phenol into o- and p-mononitrophenol (in the cold it is chiefly the p-compound which is formed). At −67°, with use of the electric spark, there is five times as much of the p-body as at −40° (B. **26**, R. 362). The o- and p-compounds are separated by distillation with steam, in which the

latter is not volatile. Phenol in presence of sulphuric acid is also nitrated by nitrogen dioxide (B. **24**, R. 722).

o- and p-Nitrophenols are obtained by heating the corresponding chlor- and brom-nitrobenzenes with caustic potash to 120°, whereas m-brom-nitrobenzene does not react under similar circumstances (p. 67). Ortho- and para-nitrophenols are likewise produced from the corresponding nitranilines by heating with alkalies (p. 93). m-Nitrophenol is formed from m-nitraniline (from ordinary dinitrobenzene) by boiling the diazo-compound with water. p-Nitrophenol has also been obtained synthetically from nitromalonic aldehyde with acetone.

o-**Nitrophenol** melts at 45° and boils at 214°; its methyl ether melts at + 9° and boils at 265°.

m-**Nitrophenol** melts at 96°; its methyl ether melts at 38° and boils at 254°.

p-**Nitrophenol** melts at 114°; its methyl ether melts at 48° and boils at 260°.

o- and m-Nitrophenols form yellow crystals; the latter is rather soluble in water. The o-body has a peculiar odor and sweet taste. Its sodium salt forms dark-red prisms.

p-*Nitrophenol* crystallizes from hot water in long, colorless needles. The potassium salt crystallizes in yellow needles with two molecules of water.

Bromine converts p-nitrophenol into dibrom-p-nitrophenol (1,4,2,6,OH in 1), melting at 141°.

PCl_5 converts o- and p-nitrophenols into o- and p-chlornitrobenzenes (p. 67).

Dinitrophenols, $(NO_2)_2C_6H_3OH$.—*α*- or [1OH, 2,4]-**Dinitrophenol**, melting at 114°, and *β*- or [1OH . 2,6]-**Dinitrophenol**, melting at 64°, are produced in the nitration of phenol and of o-*nitrophenol*. The *α*-compound can also be obtained from p-nitrophenol, as well as from m-dinitrobenzene, by means of alkaline potassium ferricyanide. The *α-methyl ether* melts at 86°. It is transformed into [$1NH_2$, 2,4]-dinitraniline by heating with ammonia.

The nitration of [1,3]-nitrophenol produces three isomeric *dinitrophenols*, melting at 104°, 134°, and 141°. Further nitration produces *trinitrophenols* and *trinitroresorcinol* (p. 161).

Trinitrophenols.—Picric Acid, $C_6H_2(NO_2)_3 . OH$, melting at 122°, is obtained by the nitration of phenol, of [1,2]- and [1,4]-nitrophenol, and of the two dinitrophenols; also, by the oxidation of symmetrical trinitrobenzene with potassium ferricyanide. Its structure is therefore 1,2,4,6 (OH in 1).

Picric acid is produced in the action of concentrated nitric acid upon various organic substances, like indigo, aniline, resins, silk, leather, and wool.

History.—Welter, in 1799, first prepared pure picric acid by nitrating silk. It was named Welter's *bitter*. Liebig called it *carbon-nitric acid*, *carbazotic acid*. Dumas analyzed it and called it *picric acid*, from πικρός, bitter. Laurent, in 1842, discovered it to be a derivative of phenol.

Properties.—Picric acid crystallizes from hot water and alcohol in yellow leaflets or prisms which possess a very bitter taste. It dissolves in 160 parts of cold water and rather readily in hot water. Its solution imparts a beautiful yellow color to silk and wool. It sublimes undecomposed when carefully heated.

Deportment.—With many hydrocarbons, like benzene, naphthalene, and anthracene, picric acid forms beautiful, crystalline derivatives, well adapted for the recognition and separation of the higher aromatic hydrocarbons.

Phosphorus pentachloride converts picric acid into trinitro-chlorbenzene, $C_6H_2(NO_2)_3$. Cl (p. 68).

Prussic acid is produced on boiling a solution of barium picrate with baryta water.

Picric acid is converted by potassium cyanide into the potassium salt of *isopurpuric* or *picrocyaminic acid*, $C_8H_4N_5O_6K$. It crystallizes in brown leaflets with green-gold lustre, and formerly appeared in commerce under the name *Grénat soluble*. It is no longer used. The free acid is not known.

Salts and Ethers.—The *potassium salt*, $C_6H_2(NO_2)_3 . OK$, crystallizes in yellow needles, soluble in 260 parts of water at 15°.

The *sodium salt* is soluble in 10 parts water at 15°, and is separated from its solution by sodium carbonate. The *ammonium salt* consists of beautiful, large needles, and is applied in explosive mixtures. All the picrates explode very violently when heated or struck.

The *methyl ester* of picric acid is produced in the nitration of anisol. It melts at 65°. The *ethyl ester* melts at 78°.

β-Trinitrophenol, melting at 96°, and *γ-Trinitrophenol*, melting at 117°, have been obtained from the dinitrophenols resulting from the nitration of m-nitrophenol.

Tetranitrophenol, melting at 130°, consists of golden yellow needles. It is produced in the oxidation of diquinoyltrioxime (see this). It is very explosive (B. **30**, 184).

Nitrocresols.—o- and p-Cresol are easily converted into dinitro-derivatives (B. **15**, 1864; **17**, 270). The [2,6]-dinitro-p-cresol, melting at 84°, has been introduced into trade in the form of its sodium salt, bearing the name *Victoria orange*, or *Safran surrogate*. It is an orange-yellow dye. It is not extensively applied as yet. When m-cresol is nitrated, it yields a *trinitrocresol*, $(NO_2)_3C_6H(CH_3)OH$, melting at 106°. This has also been formed from nitrococcic acid (see this).

Haloid Nitrophenols.—Numerous representatives of this class have been obtained by the action of the halogens upon the nitrophenols or by the nitration of the haloid phenols.

It is interesting to note that p-*Nitro-o-iodanisol*, $C_6H_3[4]NO_2[2]I[1]OCH_3$, has been prepared both in the nitration of o- as well as in that of p-iodanisol. In the latter case, therefore, a migration or wandering of the iodine atom in the nucleus has occurred (B. **29**, 997).

NITROSO-COMPOUNDS OF THE PHENOLS.

The nitroso-phenols are made: (1) by the action of nitrous acid upon phenols (Baeyer, B. **7**, 964), when the monohydric phenols yield only mononitroso-compounds; whereas dinitroso-derivatives are obtained from the dihydric meta-dioxybenzenes, like resorcinol.

(*a*) Nitrous acid, from alkali nitrite and dilute sulphuric acid or acetic acid, is allowed to act upon the phenols (B. **7**, 967; **8**, 614); (*b*) by means of the nitrites of heavy metals, which are decomposed by the phenols themselves (B. **16**, 3080); (*c*) from nitrosyl sulphuric acid, $HO . SO_2 . NO$, and phenols (A. **188**, 353; B. **21**, 429); (*d*) from amyl nitrite and sodium phenolates (B. **17**, 803).

(2) Upon boiling p-nitroso-alkylamines, like nitroso-dimethylaniline (I, 163; II, 94) with alkalies:

$$NO[4]C_6H_4[1]N(CH_3)_2 + NaOH = NO[4]C_6H_4[1]OK + HN(CH_3)_2.$$

(3) By the action of HCl-hydroxylamine upon quinones in aqueous or alcoholic solution. Free hydroxylamine reduces the quinones to hydroquinones (B. **17**, 2061). This method favors the idea that the nitrosophenols are quinone monoximes (Goldschmidt, B. **17**, 801). Hence, three constitutional formulas have been brought forward for p-nitrosophenol or quinone monoxime (Quinones, see these):

$$C_6H_4\begin{cases}OH\\NO\end{cases} \quad \text{and} \quad C_6H_4\begin{cases}O\\N.OH\end{cases} \quad \text{or} \quad C_6H_4\begin{cases}O\\N.OH\end{cases}$$

p-Nitrosophenol — Quinoxime.

p-**Nitrosophenol, Quinoxime,** crystallizes from hot water in colorless, delicate needles, which readily brown on exposure, and from ether it separates in large, greenish-brown leaflets. It is soluble in water, alcohol, and ether, and imparts to them a bright green color. When heated, it melts with decomposition, and deflagrates at 110–120°. The *sodium salt* crystallizes in red needles, containing two molecules of water of crystallization.

The methods of producing nitrosophenol from phenol with nitrous acid, and from nitroso-dialkyl anilines, argue for the nitroso-formula of the nitrosophenols; as does their oxidation to p-nitrophenol with nitric acid or with an alkaline potassium ferricyanide solution.

The quinoxime formula is supported by their formation from quinone with hydroxylamine hydrochloride and the conversion into quinodioxime, as well as by the formation of hypochlorous esters, $C_6H_4(O).NOCl$, when acted upon by bleaching lime (B. 19, 280). Further, the behavior of the related nitrosonaphthols (see these), and finally the feeble basic character of the nitrosophenols (B. 18, 3198). The reduction to p-amidophenol is in harmony with both formulas.

The nitrosophenols can be changed to nitrosoanilines (p. 94). Hydrochloric acid converts nitrosophenol into dichloramido-phenol. With nitrous acid and with hydroxylamine it yields p-diazophenol:

$$C_6H_4(OH)NO + NH_2.OH = C_6H_4(OH).N_2.OH + H_2O.$$

In a similar manner it forms azo-compounds with the amines (p. 155). Phenylhydrazine reduces it very readily to amidophenol (B. 29, R. 294). On adding a little concentrated sulphuric acid to a mixture of nitrosophenol and phenol, we obtain a dark red coloration, which changes to dark blue upon adding caustic potash (p. 141).

Quinon-dioxime will be described together with quinone (see this). *Nitroso-o-cresol*, from o-cresol and toluquinone (see this) (B. 21, 729), melts at 134°. *Nitrosothymol* melts at 160° (B. 17, 2061).

AMIDOPHENOLS.

They result from the reduction of nitrophenols, and amidophenol-derivatives, in a similar manner, from the corresponding nitrophenol-derivatives. In the case of the poly-nitrated phenols, ammonium sulphide occasions but a partial, tin and hydrochloric acid, however, a complete, reduction of the nitro-groups (p. 71). For special methods of formation, see m- and p-Amidophenol.

Deportment.—The free amidophenols decompose quite easily, especially in moist air on exposure to light.

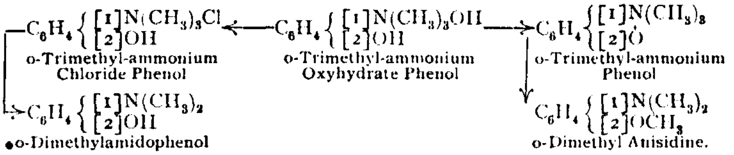
The amido-group considerably diminishes the acid character of the phenols. This class of derivatives no longer forms salts with alkalies, and only yields such compounds with the acids.

Like the o-phenylenediamines (p. 96), the o-amidophenols form heterocyclic derivatives with ease. These are anhydro-bases, the *benzoxazoles*, corresponding to the *benzimide azoles* (see these). The *benzothiazoles* (see these) are similar bodies obtained from the o-amidothiophenols.

o-Amidophenol, $NH_2[2]C_6H_4[1]OH$, melting at 170°, dissolves with difficulty in water. **o-Anisidine,** $NH_2[2]C_6H_4[1]OCH_3$, boils at 218°. *Oxethyl-o-amidophenol*, $HOCH_2.CH_2NH[2]C_6H_4[1]OCH_3$, boils at 290–310°.

Methylation of the Amido-group of o-Amidophenol (B. 23, 246).—When o-amidophenol in methyl alcohol is treated with methyl iodide and caustic potash, and later with hydrogen iodide, there results the iodide of an ammonium base, which moist silver oxide

changes to the ammonium hydroxide. The latter loses water at 105° and changes to a cyclic ammonium derivative similar to betaïne: o-**Trimethyl-ammonium Phenol**, which, heated to higher temperatures, rearranges itself into o-**dimethylanisidine**. The hydrochloride of the ammonium base breaks down upon distillation into methyl chloride and o-**dimethylamidophenol**, melting at 45°.



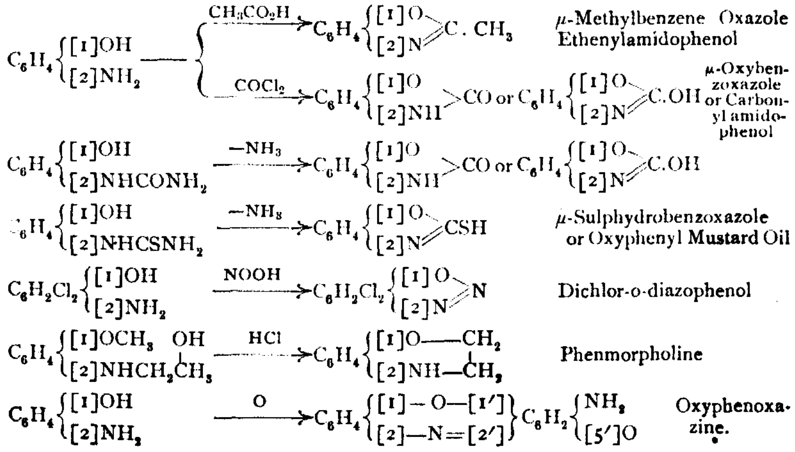
o-**Imidodiphenyl Oxide**, *Phenoxazine*, $O<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>NH$, will be described together with thiodiphenylamine, hydrophenazine and phenazine (p. 96) under the heterocyclic compounds. (Compare also Pyrocatechol, p. 159.)

o-*Oxethylanisidine*, $HO.CH_2.CH_2.NH[2]C_6H_4[1]OCH_3$, from o-anisidine and ethylene chlorhydrin (1, 301) (compare Condensations of the o-Amidophenols), boils at 305°.

o-*Oxyphenyl Urea*, $NH_2CONH[2]C_6H_4[1]OH$, melts at 154°. o-*Oxyphenylthiurea*, $NH_2CSNH[2]C_6H_4[1]OH$, melts at 161°. (Compare Condensations of the o-Amidophenols.)

The Condensations of the o-Amidophenols.—Like the o-diamines (p. 95) and o-amidothiophenols (p. 157), the o-amidophenols are highly suitable for the formation of o-condensation products:

(1) *Benzoxazoles* result by the union of o-amidophenol with carboxylic acids; thus, with acetic acid the product is *μ-methylbenzoxazole*. (2) With phosgene it is *μ-oxybenzoxazole*, or *carbonyl amidophenol*. (3) The latter body is also produced upon heating o-oxyphenyl urea (see above), and in like manner (4) o-oxyphenylthiurea yields o-*oxyphenyl mustard oil*. (5) Nitrous acid converts several substituted o-amidophenols into rather stable *diazides*; thus, *dichlor* o-*amidophenol* becomes *dichlor*-o-*diazophenol*. (6) o-Oxyethyl-anisidine, when heated with hydrochloric acid, becomes *phenmorpholine* (see this). (7) Oxidants convert o-amidophenol into *oxyphenoxazine* (see this). (8) o-Amidophenol and pyrocatechol condense to phenoxazine (see this):



m-Amidophenol, melting at 122°, is obtained from m-nitrophenol (B. 11, 2101),

from the oxamic acid derivative of m-phenylenediamine (B. **28**, R. 30), and by heating resorcinol to 200° with ammonium chloride and aqueous ammonia. In this way the alkylamines yield the alkyl-m-amido-phenols. The latter can also be obtained from the dialkyl-aniline-m-sulphonic acids (B. **22**, 622).

Monoalkyl-m-*amidophenols* (B. **27**, R. 953).—*Dimethyl*-m-*amidophenol* melts at 87°; *diethyl*-m-*amidophenol* boils at 280°. m-Amidophenol and its alkyl derivatives are employed in the preparation of *rhodamine dyes*.

Consult B. **29**, 501, for the action of phosgene upon the alkyl m-amidophenols. *Trimethyl*-m-*amidophenol*, $C_6H_4[1]OH[3]N(CH_3)_3OH$—see B. **29**, 1533.

p-**Amidophenol** melts at 184° with decomposition and sublimes. It results (1) from p-nitrophenol; (2) from β-phenylhydroxylamine (p. 70); (3) by the action of the electric current upon nitrobenzene in strong sulphuric acid solution; its formation here is due to the rearrangement of the β-phenylhydroxylamine produced at first; (4) from [5]-amido-salicylic acid. It is oxidized to quinone by chromic acid, or by PbO_2 and sulphuric acid. Bleaching lime converts it, as well as its substitution products, into quinone chlorimides. p-Amidophenol acts the same and just as readily as phenylhydrazine upon aldehydes and ketones in dilute acetic acid (B. **27**, 3005).

p-*Amidophenetol*, p-*Phenetidine*, $NH_2[4]C_6H_4[1]OC_2H_5$, is the ethyl ether. It boils at 242°. Boiling glacial acetic acid converts it into p-*Acetamidophenetol*, $C_6H_4<^{NH.CO.CH_3}_{O.C_2H_5}$, **phenacetin**, melting at 135°, which has been applied as an antipyretic. Also p-*Ethoxyphenylsuccinimide*, **Pyrantin**, $(CH_2CO)_2NC_6H_4OC_2H_5$, melting at 155°, which, it is claimed, does not have the unpleasant action or after-effects peculiar to phenacetin (B. **29**, 84). p-*Phenetolcarbamide*, $NH_2CO.NH[4]C_6H_4[1]OC_2H_5$ (B. **28**, R. 78, 83), has a very sweet taste. See p. 158 for Diamido-diphenyloxide-amidophenylsulphides.

m-*Oxydiphenylamine*, $C_6H_5NH[3]C_6H_4[1]OH$, melting at 82° and boiling at 340°, and p-*Oxydiphenylamine*, melting at 70° and boiling at 330°, are formed on heating resorcinol (p. 160) and hydroquinone with aniline and zinc chloride (B. **22**, 2909). The oxydiphenylamines are intimately related to the indophenol-dyes. (See Quinones.)

Diamidophenols.—[2,4]-*Diamidophenol*, $(NH_2)_2[2,4]C_6H_3[1]OH$, is obtained from [2,4]-dinitrophenol, and by the electrolytic reduction of m-dinitrobenzene or m-nitroaniline in sulphuric acid (B. **26**, 1848). The free base is very unstable, and its salts have been used as developers in photography under the name **amidol**. m-*Anilido*-p-*phenitidine*, $C_6H_5NH[3]C_6H_3\begin{cases}[1]OC_2H_5\\ [4]NH_2\end{cases}$; see p. 155, under Hydrazine Phenols, for its formation.

Picramic Acid, [2]-*Amido*-[3,4]-*dinitrophenol*, $C_6H_2(NH_2).(NO_2)_2.OH$, is obtained by evaporating ammonium picrate in alcoholic solution with ammonium sulphide. It forms red needles, which melt at 165°.

[2,4,6]-**Triamidophenol**, $C_6H_2(NH_2)_3.OH$, is obtained from picric acid by the action of phosphorus iodide, or by tin and hydrochloric acid (B. **16**, 2400). When set free from its salts, it decomposes very quickly. Its salts, with three equivalents of acids, crystallize well. The HI-salt, $C_6H_3O(NH_2)_3.3HI$, crystallizes in colorless needles. These salts color water which is faintly alkaline, and even spring water, a beautiful blue. If ferric chloride be added to the solution of the hydrochloride, it will become deep blue in color, and brown-blue needles with metallic lustre will separate; they are *HCl-amido-di-imido-phenol*, or diamidoquinone-imide (see this), which dissolves in water with a beautiful blue color.

An isomeric triamidophenol has been prepared by reducing diquinoyltrioxime (B. **30**, 183).

[3,3,4,5]-*Tetramidoanisol*, $(NH_2)_4C_6HOCH_3$ (B. **25**, 282).

Diazophenols.—*Phenoldiazochlorides*, $HO.C_6H_4N_2Cl$, result from the action of nitrous acid upon the hydrochlorides of the amidophenols. The free diazohydrates of the o- and p-amidophenols seem to become anhydrides, in that the second affinity of the diazo-groups joins itself to the phenol hydrogen (B. **29**, 1522):

$$C_6H_4\begin{cases}N_2\\ O\end{cases}\!\!>, \qquad C_6H_2Cl_2\begin{cases}N_2\\ O\end{cases}\!\!>, \qquad C_6H_3(NO_2)\begin{cases}N_2\\ O\end{cases}\!\!>.$$

p-*Diazophenol Cyanide*, $HO[4]C_6H_4N_2 . CN$, from the action of potassium cyanide on the chloride, consists of yellow needles. Caustic potash saponifies it to the potassium salt of *diazophenolcarboxylic acid*, $HO . C_6H_4N_2COOH$. *Dibromphenoldiazo sulphonic Acid*, $C_6H_2Br_2(OH)N_2SO_3H + 2H_2O$, can be isolated from its potassium salt produced from the interaction of potassium sulphite and dibromphenoldiazochloride.

p-*Phenoldiazomercaptan Hydrosulphide*, $C_6H_4(OH) . N_2SH . SH_2$, from the action of hydrogen sulphide upon diazophenol solutions, consists of red needles melting at 75° with decomposition (B. **28**, 3250).

Hydrazine Phenols.—The free bodies are exceedingly unstable.

o-*Hydrazine Anisol*, $NH_2NH[2]C_6H_4[1]OCH_3$, melts at 43° and boils at 240° (A. **221**, 314). Benzene-p-hydrazine phenol ethers result from the reduction of the alkyl ethers of the oxyazobenzenes or azophenols; they show the semidine rearrangement when acted upon with stannous chloride and hydrochloric acid (p. 117). Thus, *benzene-p-hydrazophenetol* changes to m-ethoxy-o-amidodiphenylamine (B. **27**, 2700; **28**, R. 753; **29**, 2680):

$$C_6H_5NHNH[1]C_6H_4[4]OC_2H_5 \longrightarrow \left.\begin{matrix} C_6H_5NH[1] \\ NH_2[2] \end{matrix}\right\} C_6H_3[5]OC_2H_5.$$

Azophenols, Oxyazobenzenes.—*Formation.* (1) From diazo-salts and monohydric phenols, m-dioxybenzenes, m-amidophenols, and m-phenolsulphonic acids:

$$C_6H_5N = N . NO_3 + C_6H_5OH = C_6H_5N = N[1]C_6H_4[4]OH.$$

The solution of the diazo-salt is allowed to run into the alkaline phenol solution while cooling and stirring. Phenoldisazobenzene is produced together with phenolazobenzene.

As with the amidoazo-compounds, the entering diazo-group arranges itself in the phenols in the p-position, and when this is already occupied it takes the o-position with reference to the hydroxyl group (B. **17**, 876; **21**, R. 814).

(2) By heating the diazoamidobenzenes with monohydric phenols, and also with resorcinol (B. **20**, 372, 904, 1577):

$$C_6H_5N_2 . NH . C_6H_5 + C_6H_5 . OH = C_6H_5 . N_2 . C_6H_4OH + C_6H_5 . NH_2.$$

(3) By the molecular rearrangement induced by heating azoxybenzenes with sulphuric acid (B. **14**, 2617):

$$\begin{matrix} C_6H_5 . N \\ C_6H_5 . N \end{matrix}\!\!>\!O \longrightarrow C_6H_5 . N_2 . C_6H_4OH$$

Azoxybenzene — Oxyazobenzene.

(4) By reduction of the nitrophenols in alcoholic potassium hydroxide solution.

(5) By the action of anilines upon nitrosophenols.

Constitution.—The oxyazo-compounds, containing hydroxyl in the ortho-position to the azo-group, are probably quinone-hydrazones:

$$C_6H_4\left\{\begin{matrix}[1]OH \\ [2]N = N . C_6H_5\end{matrix}\right. \longrightarrow C_6H_4\left\{\begin{matrix}[1] : O \\ [2] : N—NHC_6H_5\end{matrix}\right. \text{ or } C_6H_4\left\{\begin{matrix}[1]O \\ [2]\,N—NH . C_6H_5\end{matrix}\right.$$

o-Oxyazobenzene — Quinonephenyl-hydrazone.

This seems to be evident both from their cryoscopic and chemical behavior (B. **28**, 2415; **29**, 2361); compare also naphthoquinonehydrazones.

p-**Oxyazobenzene, Benzene-p-azophenol**, $C_6H_5N = N[1]C_6H_4[4]OH$, melting at 148°, crystallizes in orange-yellow needles. It is produced by the methods mentioned in connection with oxyazo-derivatives; treated with phosphorus pentachloride, and then with water, it is converted into the phosphoric ester, $PO(OC_6H_4N_2C_6H_5)_3$, melting at 148° (B. **24**, 365). **Benzene-p-azophenetol** melts at 77° (B. **25**, 994). p-**Azophenol**, $HO[4]C_6H_4[1]N_2[1]C_6H_4[4]OH$, melting at 204°, consists of light-brown crystals. It is produced:

(1) By fusing p-nitro- and nitroso-phenol with caustic alkali.

(2) By the pairing of diazobenzene nitrate with phenol.

(3) From p-oxyazobenzene-sulphonic acid (B. **15**, 3037).

See B. **17**, 351, for the azo- and diazo-derivatives of the cresols.

The sulpho-acids of the oxyazobenzenes are *dyes*—*e. g.*, p-**Sulpho-benzene-p-azo-phenol**, $SO_3H[4]C_6H_4[1]N = N[2]C_6H_4[4]OH$, from p-oxyazobenzene and sulphuric acid, and from p-diazobenzene-sulphonic acid by means of sodium phenate, is *tropæoline* Y (from yellow) of commerce (B. **11**, 2192). Also compare resorcinol.

Sulphonic Acids of Phenol.—The sulphonation of phenol proceeds with the replacement of the o- and p-hydrogen atoms, just as in the nitration process (the sulpho-groups enter the meta-position with reference to one another):

$$C_6H_5OH \left\{ \begin{matrix} \longrightarrow C_6H_4 \left\{ \begin{matrix} [1]OH \\ [2]SO_3H \end{matrix} \right. \\ \longrightarrow C_6H_4 \left\{ \begin{matrix} [1]OH \\ [4]SO_3H \end{matrix} \right. \end{matrix} \right\} \longrightarrow C_6H_3 \left\{ \begin{matrix} [1]OH \\ [2]SO_3H \\ [4]SO_3H \end{matrix} \right. \longrightarrow C_6H_2 \left\{ \begin{matrix} [1]OH \\ [2]SO_3H \\ [4]SO_3H \\ [6]SO_3H. \end{matrix} \right.$$

o- and p-**Phenolsulphonic Acids** are formed when phenol dissolves in concentrated sulphuric acid; at medium temperatures the former is the more abundant, but readily passes into the *para-* on the application of heat, or even upon boiling with water. o-Phenetolsulphonic acid is just as easily changed to the p-acid by heating it to 100° (B. **27**, R. 591).

The acids are separated through their potassium salts. On allowing to crystallize the potassium salt of the *para*-acid first separates in hexagonal plates; later the ortho-salt, $C_6H_4(OH) . SO_3K + 2H_2O$, crystallizes out in prisms, which soon effloresce on exposure (A. **205**, 64).

The free acids can be obtained in crystalline form by the slow evaporation of their aqueous solution. The aqueous solution of the ortho-acid is applied as an antiseptic under the name of **aseptol** (B. **18**, R. 506). The para-acid yields quinone if its sodium salts be oxidized with MnO_2 and sulphuric acid. When the ortho-acid is fused with KOH at 310° it yields pyrocatechin—o-dioxybenzene; the para-acid does not react at 320°, and at higher temperatures yields diphenols. (See Diphenyl.)

The iodation of the para-acid produces [2,6] *Di-iod-phenolsulphonic Acid*, $C_6H_2I_2 . (OH) . SO_3H$. This is applied as an antiseptic, bearing the name **sozo-iodol** (B. **21**, R. 250).

Meta-phenolsulphonic Acid [1,3] is produced when meta-benzene-disulphonic acid (p. 135) is heated to 170–180° with aqueous potassium hydroxide (B. **9**, 969). The free acid contains two molecules of H_2O. Fusion with potassium hydroxide at 250° converts it into resorcinol [1,3]. When para-benzene-disulphonic acid is heated with caustic alkali, meta-phenol-sulphonic acid is also produced at first, but it yields resorcinol later.

Phenol-[2,4]-disulphonic Acid results from the action of an excess of sulphuric acid upon phenol, also upon [1,2]- and [1,4]-phenol-sulphonic acid. The solutions of the acid and its salts are colored a dark red by ferric chloride.

Phenol-[2,4,6]-trisulphonic Acid is obtained when concentrated sulphuric acid and P_2O_5 act upon phenol. It crystallizes in thick prisms with $3\frac{1}{2}H_2O$.

See B. **28**, R. 378, 399, for the *amidophenol-sulphonic acids.*

THIO-DERIVATIVES OF PHENOL.

Mercaptans.—Thiophenol, *Phenylmercaptan* [*Phenthiol*], C_6H_5SH, boiling at 168°, with sp. gravity 1.078 (14°), is a mobile, ill-smelling liquid. It is made (1) by letting P_2S_5 act upon phenol (Z. f. Ch. 1867, 193); (2) by distilling sodium benzene sulphonate with potassium sulphydrate (B. **17**, 2080); (3) from phenyldithiocarbonic

esters (see below). It manifests great tendency to throw off hydrogen and become phenyldisulphide; hence it often acts as a reducing agent (compare B. **29**, R. 979). *Mercury Thiophenate*, $(C_6H_5S)_2Hg$. *Thiophenyl Acetal*, $C_6H_5 . S . CH_2 . CH(OC_2H_5)_2$, boils at 273° (B. **24**, 160). *Thiophenylacetone* melts at 34° and boils at 266° (B. **24**, 163). Consult B. **24**, 234; **28**, 1120; A. **253**, 161, for mercaptal (1, 204) and mercaptol derivatives of thiophenol. *Phenyl Orthothioformic Ester*, $C_6H_5S . CO_2 . C_2H_5$, boils at 260° (B. **19**, 1228). *Phenyldithiocarbonic Ester*, $C_6H_5S . CSOR$, is formed from diazobenzene chloride and represents a common reaction. It yields thiophenol when saponified. This is the most convenient way of preparing thiophenols (B. **21**, R. 915). *Diazobenzene Thiophenyl Ester*, $C_6H_5N_2 . SC_2H_5$, an oil, is produced from diazobenzene chloride and phenylmercaptan (B. **28**, 3237).

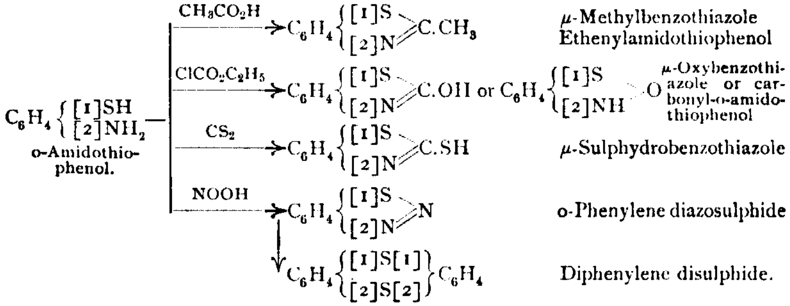
o-*Thiocresol* melts at 15° and boils at 188°; the m-body is a liquid boiling at 195–205° while the p-compound melts at 43° and boils at 194°. *Thiocymene*, $(CH_3)(C_3H_7)C_6H_3SH$ (see carvacrol, p. 145).

Mention should be made of o-amidothiophenol, one of the numerous substitution products of thiophenol, because of its heterocyclic condensation products.

o-Amido-thiophenol, $NH_2[2]C_6H_4[1]SH$, is obtained from ortho-nitro-benzene-sulphonic chloride by reduction with tin and hydrochloric acid. A better method to pursue is to fuse benzenyl-o-amidothiophenol with caustic potash (B. **20**, 2259). It melts at 26° and boils at 234°.

m-*Amidothiophenol* (B. **27**, 2816).

The condensations of the o-Amidothiophenols (compare o-diamines, p. 95 and o-amidophenols (p. 153). (1) *Benzothiazoles* are formed on heating o-amidothiophenol with carboxylic acids, acid chlorides, or acid anhydrides. (2) o-Amidothiophenol, by the action of chlorcarbonic esters, forms *μ-oxybenzothiazole* or *carbonylamidothiophenol*. (3) Carbon disulphide produces *μ-sulphydrobenzothiazole* (see this). (4) Nitrous acid converts o-amidothiophenol into *o-phenylene diazosulphide* (see this); at 200–220° this becomes *diphenylene disulphide*:



Phenylsulphocarbazine (p. 127) is also a heterocyclic derivative of o-amidothiophenol. See p. 160 for the condensation of o-amidothiophenol with pyrocatechol to *thiodiphenylamine*.

Sulphides.—*Phenyl Disulphide*, $(C_6H_5)_2S_2$, melting at 61° and boiling at 310°, results from the oxidation of thiophenol with a chromic acid mixture or in ammoniacal solution by the oxygen of the air; by the action of iodine upon aqueous potassium thiophenate; by heating thiophenol with benzene sulphinic acid; by heating thiophenol or phenylsulphide with sulphur, etc. Reducing agents decompose it into two molecules of thiophenol, and alcoholic potash breaks it down into potassium thiophenate and potassium benzene sulphinate.

Phenyl Sulphide, $(C_6H_5)_2S$, Benzene sulphide, a colorless liquid with an odor resembling that of leeks, boils at 292° and has a specific gravity of 1.12. It is formed (1) by distilling phenol with P_2S_5 (along with thiophenol); (2) in the distillation of sodium benzene sulphonate, as well as in the action of benzene diazochloride upon sodium thiophenate with P_2S_5 (B. **23**, 2471); (3) on heating sulphur with diphenyl-

sulphone (method of preparation), into which it is also converted by oxidants (B. **26**, 2816); (4) upon heating mercury diphenyl with sulphur (B. **27**, 1771); (5) phenyl sulphide and its homologues are also readily prepared by heating aromatic lead mercaptides with haloid benzenes (the bromides are the best adapted for this purpose) (B. **28**, 2322). *Diphenylene sulphide* or *dibenzothiophene* (see this) is produced on conducting the vapors of phenylsulphide through a tube heated to redness.

Amidophenyl Sulphides or Thioanilines.—*Formation:* (1) These compounds result when nitrothiophenyls are reduced (comp. B. **29**, 2362); (2) from anilines by boiling the latter with sulphur and lead oxide (B. **4**, 384). Sulphur chloride converts the dialkylanilines into sym.-p-tetra-alkyl-diamidophenyl sulphides. Silver nitrate and ammonia desulphurize the tetra-alkyl compounds, with the formation of sym. p-tetra-alkyl-diamidodiphenylene oxides—*e. g.*, $O[C_6H_4[4].N(CH_3)_2]_2$ (B. **21**, 050). Upon heating methyl-thio-anilines—*e. g.*, thio-p-toluidine—with sulphur to higher temperatures, thiazole derivatives, like *dehydrothiotoluidine* (see benzothiazole), are produced.

p-*Diamidodiphenyl Sulphide*, $S<{C_6H_4.NH_2 \atop C_6H_4.NH_2}$, *Thioaniline*, melts at 105°. o-*Diamidodiphenyl Sulphide* melts at 93° (B. **27**, 2807). See B. **29**, 2774 for isomeric thioanilines, melting at 80° and 86°.

Thio-p-*toluidine*, $S<{C_6H_3(CH_3).NH_2 \atop C_6H_3(CH_3).NH_2}$, Diamidoditolyl Sulphide, melts at 103.° The sodium salts of thio- and dithio-toluidine sulphonic acids dye unmordanted cotton (B. **21**, R. 877). They are, therefore, so-called substantive cotton dyes.

The bis-diazo salts of thio-p-toluidine combine with naphthylamine-sulphonic acids and yield diazo dyes of a brown-red color (B. **20**, 664).

Thiodiphenylimides.—*Thiodiphenylamine*, $S\left\{{[1]C_6H_4[2] \atop [1]C_6H_4[2]}\right\}NH$, is the simplest of these heterocyclic bodies. *Methylene blue*, a most valuable dye, is derived from it. The thiophenylamine group will be discussed later with the hetero six-ring compounds.

Thioanisol, $S(C_6H_4OCH_3)_2$, melting at 46°, and allied bodies are formed when thionyl chloride or sulphur chloride with aluminium chloride acts upon the phenol-ethers (A. **27**, 2540).

Phenylselenides and *tellurides* are quite readily obtained from the mercury diphenyl compounds by the action of selenium and tellurium.

Diphenylselenide, $(C_6H_5)_2Se$, also results upon heating selenium with diphenylsulphone. Sulphur dioxide escapes at the same time. It boils at 163° (14 mm.). Further action of selenium produces *diphenyldiselenide*, $(C_6H_5)_2Se_2$, melting at 63° and boiling at 203° (11 mm.). Reduction changes it to two molecules of *phenylselenium hydrate*, C_6H_5SeH, melting at 183°. *Diphenyltelluride*, $(C_6H_5)_2Te$, boils at 174° (10 mm.)—see B. **28**, 1670; **29**, 428.

DIHYDRIC PHENOLS.

Several representatives of this family occur in plants, or have been obtained as decomposition products of plant substances. *Resorcinol* or m-dioxybenzene is especially important from a technical standpoint.

The *general methods of formation* are like those of the corresponding monohydric phenols—(1) by fusing monohalogen phenols, halogen benzenesulphonic acids, phenolsulphonic acids, and benzenedisulphonic acids with potassium hydroxide (pp. 135, 149, 156); (2) by diazotizing the amido-phenols; and (3) by the dry distillation of aromatic dioxyacids alone or with lime or baryta.

(4) o- and p-Dioxybenzenes also result from the careful reduction of their corresponding quinones.

Deportment.—Their behavior is largely dependent upon the position

of the two hydroxyl groups with reference to one another.' The three simplest dioxybenzenes:

Pyrocatechol [1,2], *Resorcinol* [1,3], *Hydroquinone* [1,4], are, therefore, typical representatives of the three groups of dihydric phenols. The deportment of such bodies can be fully illustrated through them. The dihydric phenols can be changed by chlorine to *hydroaromatic ketochlorides*, whose carbon ring may be readily ruptured (see p. 44). Chloroform and caustic potash convert them into dioxyaldehydes, while they yield dioxycarboxylic acids with carbon tetrachloride and caustic potash.

Pyrocatechin Group.—All o-dioxybenzenes are colored green by ferric chloride. They are further distinguished from the m- and p-compounds by their ability to readily exchange their hydroxyl hydrogen atoms and thus form cyclic esters.

Pyrocatechin, Pyrocatechol. o-*Dioxybenzene*, [1,2-*Phendiol*] $C_6H_4[1,2](OH)_2$, melting at 104° and boiling at 245°, was first (Reinsch, 1839) obtained in the distillation of catechine (the juice of *Mimosa catechu*), and also from *Moringa tannic acid.*

It is produced in fusing many resins with caustic potash. It occurs in *kino*, the dried juice of different kinds of *Pterocarpus*, *Butea*, and *Eucalyptus*, in beechwood tar, and has been obtained as a by-product in the manufacture of paraffin from bituminous shales at the Messel mine, near Darmstadt, etc. *Pyrocatechol-sulphuric Acid* occurs in the urine of the horse and in that of man. It is artificially made (1) by oxidizing phenol with hydrogen peroxide; (2) by the distillation of protocatechuic acid, or [$1CO_2H$, 3,4]-dioxybenzoic acid; (3) by fusing [1,2]-chlorphenol, [1,2]-bromphenol (B. **27**, R. 957, D. P. 76,597), [1,2]-benzene disulphonic acid, and [1,2]-phenolsulphonic acid with caustic potash; (4) by heating guaiacol pyrocatechol monomethyl ether (see this) to 200° with hydriodic acid.

On exposure to the air its alkaline solutions assume a green, then brown, and finally a black color. Lead acetate throws out a white precipitate, $PbC_6H_4O_2$, from its aqueous solution. Neither resorcinol nor hydroquinone shows this reaction. Pyrocatechin reduces cold silver solutions and alkaline copper solutions. The application of heat is required in the latter case. Pyrocatechin in glacial acetic acid solution is converted by chlorine into tetrachlorpyrocatechin, tetrachlor-o-quinone (p. 169), and *hexachlor*-o-*diketo*-R-*hexene* (p. 45). In nitrous acid to *dioxytartaric acid*. Consult p. 160 for the heterocyclic formations obtainable from pyrocatechol. Heated with phthalic anhydride and sulphuric acid, it yields *alizarine* (see this) and *hystazarine* (see this). Compare protocatechuic aldehyde and protocatechuic acid.

Ethers.—The *monomethyl ether*, $HO[1]C_6H_4[2]OCH_3$, melting at 28° and boiling at 250°, **Guaiacol**, occurs in the creosote from beechwood tar (B. **28**, R. 156). It is produced on heating pyrocatechin with potassium hydroxide and potassium methyl sulphate to 180°, as well as by heating calcium vanillate, and from veratrol (B. **28**, R. 362). Ferric chloride gives its alcoholic solution an emerald-green color (see vanillin).

Dimethyl ether, **Veratrol**, $C_6H_4[1,2](OCH_3)_2$, melting at 15° and boiling at 205°, is prepared by treating the potassium salt of the monomethyl ether with CH_3I, and by distilling vetraric acid with lime. The *ethylene ester* boils at 216° (A. **280**, 205).

Pyrocatechin sulphite boils at 210–211° (B. **27**, 2752); *pyrocatechin chlorphosphine* melts at 130°; *pyrocatechin oxychlorphosphin* melts at 35° (B. **27**, 2569) (see below). *Diacetyl ester*, $C_6H_4[1,2](OCOCH_3)_2$.

The *carbonic ester*, $C_6H_4\left\{\begin{matrix}[1]O\\ [2]O\end{matrix}\right.\!\!>CO$, results from the action of chlorcarbonic ester upon pyrocatechin, melts at 118° and boils at 227° (B. **13**, 697; A. **226**, 84). *Monobenzoyl ester* melts at 130° (B. **26**, 1076). *Dibenzoyl ester* melts at 84° (A. **210**, 261).

Hetero-ring Formations from Pyrocatechol.—By the replacement of both

hydroxyl hydrogen atoms of pyrocatechol *cyclic esters* are formed with $SOCl_2$, PCl_3, $POCl_3$, $COCl_2$, and ethylene bromide. o-Phenylenediamine, o-amidophenol, and o-amidothiophenol condense with pyrocatechin, forming *phenazine*, *phenoxazine*, and *thiodiphenylamine*:

$C_6H_4\left\{\begin{matrix}[1]OH\\ [2]OH\end{matrix}\right.$ —

Reagent	Product	Name
$SOCl_2$	$\to C_6H_4\left\{\begin{matrix}[1]O\\ [2]O\end{matrix}\right\rangle SO$	Pyrocatechol Sulphite
PCl_3	$\to C_6H_4\left\{\begin{matrix}[1]O\\ [2]O\end{matrix}\right\rangle PCl$	Pyrocatechol Chlorphosphine
$POCl_3$	$\to C_6H_4\left\{\begin{matrix}[1]O\\ [2]O\end{matrix}\right\rangle POCl$	Pyrocatechol Oxychlorphosphine
$COCl_2$	$\to C_6H_4\left\{\begin{matrix}[1]O\\ [2]O\end{matrix}\right\rangle CO$	Pyrocatechol Carbonate
$BrCH_2.CH_2Br$	$\to C_6H_4\left\{\begin{matrix}[1]O-CH_2\\ [2]O-CH_2\end{matrix}\right.$	Pyrocatechol Ethylene Ether
$C_6H_4[1,2](NH_2)_2$	$\to C_6H_4\left\{\begin{matrix}[1]-N-[1]\\ [2]-N-[2]\end{matrix}\right\}C_6H_4$	Phenazine
$NH_2[2]C_6H_4[1]OH$	$\to C_6H_4\left\{\begin{matrix}[1]-O-[1]\\ [2]-NH-[2]\end{matrix}\right\}C_6H_4$	Phenoxazine
$NH_2[2]C_6H_4[1]SH$	$\to C_6H_4\left\{\begin{matrix}[1]-S-[1]\\ [2]-NH-[2]\end{matrix}\right\}C_6H_4$	Thiodiphenylamine.

Homologous Pyrocatechols.—*Isohomopyrocatechol*, $CH_3[1]C_6H_3[2,3](OH)_2$, melts at 47° (B. **24**, 4137). *Homopyrocatechol*, $CH_3[1]C_6H_3[3,4](OH)_2$, melting at 51° and boiling at 251°, occurs in the form of its 3-methyl ether as **creosol**, $CH_3[1]C_6H_3[3](OCH_3)[4]OH$, boiling at 221°, in beechwood tar, together with phloral (B. **14**, 2005).

Creosol is also formed together with guaiacol (see above) in the distillation of guaiacol resin. Higher homologues of pyrocatechol have been obtained by treating pyrocatechol with aliphatic alcohols and zinc chloride (B. **28**, R. 312; D. P. 78,882).

Monothiopyrocatechol, $C_6H_4[1,2](SH)(OH)$, melting at + 5° and boiling at 217°, results from the reduction of *diphenoldisulphide*, $[C_6H_4OH]_2S_2$, produced on heating sodium phenoxide with sulphur.

Diphenylene Disulphide, or *Thianthrene*, $C_6H_4\left\{\begin{matrix}[1]S[1]\\ [2]S[2]\end{matrix}\right\}C_6H_4$, melting at 158° and boiling at 360°, should be regarded as a derivative of dithiopyrocatechol, $C_6H_4(SH)_2$. It is made by boiling phenylsulphide with sulphur, also from benzene, SCl_2, and aluminium chloride, as well as by heating phenylene diazosulphide (p. 157). Oxidation converts it into a *disulphone*, $C_6H_4(SO_2)_2C_6H_4$. When the latter is heated with selenium *Diphenylene Diselenide*, selenanthrene, $C_6H_4:(Se_2):C_6H_4$, melting at 181° and boiling at 223° (11 mm.), results (B. **29**, 435, 443).

Resorcinol Group.—Resorcinol and many of its homologues combine with phthalic anhydride, the products being the ***fluoresceïns*** (see these). The aqueous solutions of the m-dioxybenzenes are colored *dark violet* by ferric chloride.

Resorcinol, $C_6H_4[1,3](OH)_2$, melting at 118° and boiling at 276°, is produced from *Galbanum*, *Asafœtida*, and other resins upon heating them with potash, as well as by distilling the extract of Brazil-wood. It can also be obtained from many m-disubstitution-products of benzene, such as [1,3]-chlor- and iodphenol, [1,3]-phenolsulphonic acid, [1,3]-benzene-disulphonic acid, etc., on fusing them with potash or soda at 230–280°; by the same method from *umbelliferone*.

Even o- and p-compounds (B. **7**, 1175; **8**, 365), especially when fused at high temperatures with caustic alkali, yield resorcinol; hence the potash fusion is not available in the determination of position (p. 149). Resor-

cinol is made on a technical scale from m-benzene-disulphonic acid (J. pr. Ch. [2] **20**, 319).

Properties and Deportment.—Resorcinol crystallizes in rhombic prisms or plates. It dissolves readily in water, alcohol, and ether, but not in chloroform and carbon disulphide. It possesses a sweet taste. Lead acetate does not precipitate its aqueous solution (distinction from pyrocatechin).

Sodium amalgam reduces resorcinol to dihydroresorcin (A. **278**, 20), or *m-diketohexamethylene* (B. **27**, 2129). Bromine precipitates it from aqueous solution as *tribromresorcinol*, melting at 111°, while chlorine converts it in glacial acetic acid solution finally into *heptachlor-resorcinol* (p. 46) (B. **26**, 498), which can be easily decomposed. Fusion with caustic soda produces phloroglucin, pyrocatechol, and *diresorcinol*, $(HO)_2C_6H_3 - C_6H_3(OH)_2$ (B. **26**, R. 233). The chlorhydrate of a *triresorcinol*, $C_{18}H_{14}O_4$ (A. **289**, 61), is formed when resorcinol is heated with hydrochloric acid.

Fluoresceïn is produced when resorcinol is heated with phthalic anhydride.

If resorcinol be heated with sodium nitrite, it forms a deep-blue dye, soluble in water. Acids turn this red (B. **17**, 2617). It is used as an indicator under the name of *lacmoid* (B. **18**, R. 126). Nitric acid, containing nitrous acid, converts resorcin into two dyes,—*resorufin* and *resazurin*,—derivatives of phenoxazine (see this) (B. **23**, 718).

When diazo-salts act upon aqueous or alkaline resorcinol solutions, azodyes and disazodyes are produced; thus, with diazobenzene nitrate or chloride the products are: *Benzeneazoresorcinol*, $(C_6H_5N_2)C_6H_3(OH)_2$, *a-* and *β-diazobenzene-disazoresorcinol*, $(C_6H_5N_2)_2C_6H_2(OH)_2$ (B. **15**, 2816; **16**, 2858; **17**, 880); while with the diazochloride of amidoazobenzene there results *azobenzene-azo-resorcinol*, $C_6H_5N_2 . C_6H_4N_2 . C_6H_3(OH)_2$ (B. **15**, 2817).

Ethers and Esters.—The *monomethyl ether* boils at 243° (B. **16**, 151). The *dimethyl ether* boils at 214° (B. **10**, 868). The *diacetyl ester* boils at 278° (B. **16**, 552). The *dicarbonic ester*, $C_6H_4(OCO_2C_2H_5)_2$, boils at 300° (B. **13**, 697). The *dibenzoate* melts at 117° (A. **210**, 256). Resorcinol combines with the various sugars under the influence of hydrochloric acid (B. **27**, 1356).

Dinitroso-resorcinol, diquinoyldioxime, $C_6H_2[1,3](OH)_2[4,6](NO)_2$ or $C_6H_2(O)_2(N.OH)_2[1,3,2,4]$, crystallizes in yellow-brown leaflets, which detonate on heating to 115° C. (B. **20**, 3133). It occurs in commerce under the names *solid green*, or *chlorine*.

Nitric acid vapors oxidize resorcinol to *v-dinitroresorcin*, $(NO_2)_2[2,4]C_6H_2[1,3](CH)_2$, melting at 115°. *Isodinitroresorcin*, Styphnic Acid, Oxypicric Acid, $(NO_2)_2[4,6]C_6H_2[1.3](OH)_2$, melts at 212°.

When cold nitric acid acts on resorcinol and various gum-resins (galbanum, etc.), or by nitrating metanitrophenol and various dinitrophenols, we get *Trinitroresorcinol*, $(NO_2)_3[2,4,6]C_6H[1,3](OH)_2$. It melts at 175°. Ferrous sulphate and lime-water color it green (picric acid colors it blood-red). The *diethyl ester* melts at 120°.

Thioresorcinol, $C_6H_4[1,3](SH)_2$, melts at 27°, and boils at 243°. It results from the reduction of benzene-m-disulphonic chloride, and when heated with phenylisocyanate, becomes *bisphenylcarbamate*, $C_6H_4(SCONHC_6H_5)_2$, melting at 179° (B. **29**, R. 177).

Homologous Resorcinols.—Orcinol is by far the most important body among those which follow:

		M.P.	B.P.	
Orcinol,	$CH_3[1]C_6H_3[3,5](OH)_2$	107°	289°	
Cresorcin,	$CH_3[1]C_6H_3[2,4](OH)_2$	104°	269°	(B. **19**, 136).
2,6-Dioxytoluene,	$CH_3[1]C_6H_3[2,6](OH)_2$	64°	—	(B. **17**, 1963).
2,4-Dioxy-m-xylene,	$(CH_3)_2[1,3]C_6H_2[2,4](OH)_2$	147°	149°	(B. **23**, 3114).
m-Xylorcin,	$(CH_3)_2[1,3]C_6H_2[4,6](OH)_2$	125°	277°	(B. **19**, 2318).
β-Orcin,	$(CH_3)_2[1,4]C_6H_2[3.5](OH)_2$	163°	279°	(B. **19**, 2318).
Mesorcin,	$(CH_3)_3[1,3,5]C_6H(OH)_2$	149°	275°	(A. **215**, 100).
Ditertiary-amylresorcinol,	$(C_5H_{11})_2C_6H_2[1,3](OH)_2$	89°	—	(B. **25**, 2653).

Orcin, *Orcinol*, $CH_3[1]C_6H_3[3,5](OH)_2$, is the most important of the six theoretically possible and known dioxytoluenes (B. **15**, 2995). It is found in many lichens of the variety *Roccella* and *Lecanora*, partly free and partly as orsellic acid, or partly as erythrine or diorsellic erythric ester. It is obtained from orsellic acid either by dry distillation or by boiling with lime.

It is obtained by fusing the extract of aloes with caustic potash. It can be prepared synthetically from 3,5-dinitro-p-toluidine and various other toluene-derivatives by the replacement of their side groups by hydroxyl groups (B. **15**, 2990).

Orcin is produced in the distillation of o-dioxyphenylacetate of silver, $(HO)_2[3,5]C_6H_3[1]CH_2.CO_2Ag$ (B. **19**, 1451), and upon heating dehydracetic acid (see vol. 1) with concentrated caustic potash (B. **26**, R. 316). Orcin crystallizes in colorless, six-sided prisms containing one molecule of water. It dissolves easily in water, alcohol, and ether, and has a sweet taste. It melts at 56°, when it contains water, but gradually loses this, and melts (dried in the desiccator) at 107°. It boils at 290°. Lead acetate precipitates its aqueous solution; ferric chloride colors it a *blue violet*. Bleaching lime causes a rapidly disappearing dark-violet coloration. It yields azo-coloring substances with diazo-compounds, and therefore has the 2OH-groups in the meta-position (p. 154). It does not form a fluoresceïn with phthalic anhydride (p. 160). Chlorine changes it, when dissolved in glacial acetic acid, into **trichlororcin**, melting at 127°. Dissolved in chloroform it is converted by the same reagent into *pentachlororcin*, or [1,3,5]-*diketo-methylpentachlor* R-*hexene* (B. **26**, 317) (p. 46).

Nitroso-orcin, $CH_3.C_6H_2(OH)_2(NO)$, consists of two modifications—dark-red crystals and bright yellow needles; the first change to the second when heated to 100–110° (B. **29**, 989).

On allowing its ammoniacal solution to stand exposed to the air, orcinol changes to orceïn, $C_{28}H_{24}N_2O_7$ (B. **23**, R. 647), which separates out in the form of a reddish-brown amorphous powder. It dissolves in alcohol and alkalies with a dark-red color, and is reprecipitated by acids. Orceïn forms red lac-dyes with metallic oxides. It is the chief constituent of the coloring-matter *archil* (called also *persio*, cudbear, and purpur—French) which originates from the same lichens as orcinol through the action of ammonia and air. *Litmus* is produced from the lichens *Roccella* and *Lecanora* by the action of ammonia and potassium carbonate. The concentrated blue solution of the potassium salt, when mixed with chalk or gypsum, constitutes the commercial litmus.

Iso-orcin (Cresorcin, γ-orcin), is obtained by fusing 2,4-toluene disulphonic acid with KOH.

p-*Xylorcin*, or β-*Orcin*, from m-dinitro-p-xylene, rapidly acquires a red color on exposure to air containing ammonia. It has been obtained by distillation from various lichen acids—*e. g.*, *usnic acid*. *Mesorcin*, or dioxymesitylene, is made from dinitromesitylene.

Hydroquinone Group.—The p-dioxybenzenes are usually called hydroquinones, because they are easily obtained by the reduction of the p-quinones, and just as readily reconverted into the latter by ferric chloride.

Hydroquinone, p-*Dioxybenzene*, $C_6H_4[1,4](OH)_2$, melting at 169°, was first obtained by the dry distillation of quinic acid and by digesting its aqueous solution with lead dioxide (Wöhler, A. **65**, 349):

$$C_6H_7(OH)_4COOH + O = C_6H_4(OH)_2 + CO_2 + 3H_2O.$$

It results also, together with glucose, on boiling the glucoside arbutin with dilute sulphuric acid, and occurs in *Protea mellifera* (B. **29**, R. 416).

It is further formed by the electrolytic oxidation of an alcoholic benzene solution acidulated with sulphuric acid (B. **27**, 1942), and by fusing [1,4]-iodphenol with potassium hydroxide at 180°; or from [2,5]-oxysalicylic acid, and from para-amidophenol; also in small quantities in the distillation of succinates. The most convenient method of preparing it consists in reducing quinone with sulphurous acid:

Extract the hydroquinone from the aqueous solution by shaking with ether, and purify the product by recrystallization from hot water that has passed through animal charcoal (B. **19**, 1467) and contains sulphur dioxide.

Hydroquinone is dimorphous and crystallizes in monoclinic leaflets and hexagonal prisms. It decomposes when quickly heated. It dissolves readily in water (in 17 parts at 15°), alcohol, and ether. It forms crystalline compounds with H_2S and SO_2; these are decomposed by water. Ammonia colors the aqueous solution reddish-brown. It is only in the presence of ammonia that lead acetate produces a precipitate in the solution of hydroquinone. Oxidizing agents (like ferric chloride) convert hydroquinone into quinone; quinhydrone is an intermediate product.

Hydroquinone, like quinone, forms quinone-dioxime (p. 172) (B. **22**, 1283) with hydroxylamine hydrochloride.

Hydroquinone is used as a "developer" in photography, and in therapeutics as an antifermentative and antipyretic agent.

Ethers.—**Methylhydroquinone**, $CH_3 . O[4]C_6H_4[1]OH$, is formed from methyl arbutin; and from hydroquinone by heating it with caustic potash, and methyl iodide or potassium methyl sulphate (B. **14**, 1989). It melts at 53° and boils at 247°. The *dimethyl ether* melts at 56° and boils at 205°. The *ethyl ether* melts at 66° and boils at 246°. The *diethyl ether* melts at 71°.

Hydroquinone bischlorphosphine, $C_6H_4(OPCl_2)_2$, melts at 65° and boils at 200° (65 mm.), while *hydroquinone bisoxychlorphosphine*, $C_6H_4(OPOCl_2)_2$, melts at 123° and boils at 270° (70 mm.) (B. **27**, 2568).

Hydroquinone Diacetate, $C_6H_4(O . COCH_3)_2$, melts at 123°.

Hydroquinone Dibenzoate, $C_6H_4(O . COC_6H_5)_2$, melts at 199°.

Homologous Hydroquinones are usually prepared by action of sulphur dioxide upon the homologous quinones. *Toluhydroquinone* results from the action of hot dilute sulphuric acid upon p-tolylhydroxylamine (p. 70). *Hydro-*p*-xyloquinone* bears the name *hydrophlorone*. *Dimethylhydrothymoquinone*, boiling at 249°, occurs in the ethereal oil of *Arnica montana* (A. **170**, 363). *Ditertiary-amyl-hydroquinone* results from hydroquinone and isoamylene with glacial acetic acid and sulphuric acid (B. **25**, 2650).

		M. P.
Hydrotoluquinone (B. **15**, 2981),	$(CH_3)[1]C_6H_3[2,5](OH)_2$	124° (A. **215**, 159).
Hydro-o-xyloquinone, ...	$(CH_3)_2[1,2]C_6H_2[3,6](OH)_2$	121° (B. **18**, 2673).
Hydro-m-xyloquinone, ...	$(CH_3)_2[1,3]C_6H_2[2,5](OH)_2$	150° (B. **18**, 1151).
Hydro-p-xyloquinone, ...	$(CH_3)_2[1,4]C_6H_2[2,5](OH)_2$	212° (A. **215**, 169).
Hydrocumoquinone, ...	$(CH_3)_3[1,2,4]C_6H[3,6](OH)_2$	169° (B. **18**, 1152).
Hydrothymoquinone, ...	$(CH_3)(C_3H_7)[1,4]C_6H_2[2,5](OH)_2$	139°, B. P. 290°.
Ditert. Amylhydroquinone, . .	$(C_5H_{11})_2C_6H_2[1,4](OH)_2$	185°.

Substituted Hydroquinones.—Monochlor- and monobrom-hydroquinones have been obtained by the action of concentrated hydrochloric or hydrobromic acid upon p-quinone (B. **12**, 1504). Monochlorquinone gave dichlorquinone, etc. (A. **210**, 153). Di-, tri-, and tetrachlorhydroquinones result from the corresponding chlorinated quinone by the action of SO_2.

Monochlorquinone	melts at	104°;	Monobromquinone	melts at	110°.
[2,5]-Dichlorquinone	"	166°;	[2,5]-Dibromquinone	"	186°.
[2,6]-Dichlorquinone	"	158°;	[2,6]-Dibromquinone	"	163°.
Trichlorquinone	"	134°;	Tribromquinone	"	136°.
Tetrachlorquinone	"	232°;	Tetrabromquinone	"	244°.

[1,3]-*Dinitro*- and [2,5]-*dinitrodiethylhydroquinone*, melting at 233° and 176° (A. **215**, 149), result from the nitration of hydroquinone diethylate and diacetate. They change into the same *trinitrodiethylhydroquinone*, melting at 130°, and [2,5]-*dinitrohydroquinone diacetate*, melting at 96°. The latter compound exchanges an NO_2-group very readily for $NH . C_6H_5$ (B. **24**, 3824).

Nitrohydroquinone, melting at 133°, is formed in the action of ammonium persulphate upon nitrophenol (J. pr. Ch. [2] **48**, 179). *Dinitrohydroquinone* results from dinitroarbutin and dinitrohydroquinone diacetate. Reduction changes these compounds to amidohydroquinones (B. **22**, 1656; **23**, 1211). 1,4-*Diamidohydroquinone* is obtained from the dioxime of 2,5-dioxyquinone (p. 170).

When tetrachlorquinone is digested with a diluted solution of primary sodium sulphite (A. **114**, 324) we get *dichlorhydroquinone disulphonic acid*, $C_6Cl_2\begin{cases}(OH)_2\\(SO_3H)_2\end{cases}$. Its aqueous solution is colored indigo-blue by ferric chloride. When its alkaline solution is boiled it oxidizes to *potassium euthiochronate* (p. 170).

Monthiohydroquinone, C_6H_4[1,4](OH)(SH), melting at 30° and boiling at 167° (45 mm.), results from p-diazophenol chloride and potassium xanthogenate. *Dithiohydroquinone*, C_6H_4[1,4]$(SH)_2$, melting at 98°, is obtained from p-benzene disulphonic chloride or diazophenyl disulphide. In the air it gradually oxidizes to p-*phenylene disulphide*, $[C_6H_4S_2]$ x.

TRIHYDRIC PHENOLS.

The three isomeric trioxybenzenes are known in the compounds pyrogallol, phloroglucin, and oxyhydroquinone.

Pyrogallol, *Pyrogallic Acid*, C_6H_3[1,2,3]$(OH)_3$, melting at 132°, is produced by the elimination of CO_2 from gallic acid or pyrogallocarboxylic acid, CO_2H[1]C_6H_2[3,4,5]$(OH)_3$, when heated alone, as was first observed by Scheele (1786), or, better, with water to 210°; also by fusing the two p-chlorphenol-disulphonic acids and hæmatoxylin with potassium hydroxide. It forms white leaflets or needles. It dissolves readily in water, with more difficulty in alcohol and ether. Its alkaline solution absorbs oxygen very energetically (B. **14**, 2666), turns brown and decomposes into carbon dioxide, acetic acid, and brown substances. It is used in gas analysis for the determination of oxygen. Pyrogallol quickly reduces salts of mercury, silver, and gold with precipitation of the metals, while it is oxidized to acetic and oxalic acids.

Ferrous sulphate containing ferric oxide colors its solution blue, ferric chloride red. Lead acetate precipitates white, $C_6H_6O_3 . PbO$. An iodine solution imparts a purple-red color to an aqueous or alcoholic pyrogallol solution. Gallic and tannic acids react similarly.

The *dimethyl ether* is found in beechwood creosote. It melts at 51–52° and boils at 252° (B. **11**, 333). Different oxidizing agents convert it into *cœrulignone*, a diphenyl derivative. The *trimethyl ether* melts at 47° and boils at 235° (B. **21**, 607, 2020). Bromine converts it into *xanthogallol*, $C_{18}H_{14}Br_{14}O_6$ (B. **21**, R. 626).

The *ethyl*, *diethyl*, and *triethyl ethers* melt at 95°, 79°, and 39°. The syrupy *dimethyl acetate* yields a quinone, $C_6H_2(OCH_3)_2O_2$, with chromic acid; the *triacetate* crystallizes.

Trichlorpyrogallol, $C_6Cl_3(OH)_3$, melts with decomposition at 177° (B. **20**, 2035).

Tribrompyrogallol, $C_6Br_3(OH)_3$, from pyrogallol and bromine, when digested with bromine yields *xanthogallol*, $C_{18}H_4Br_{14}O_6$, melting at 122° (A. **245**, 335). *Methylpyrogalloldimethyl ether*, $CH_3 . C_6H_2(OH)(OCH_3)_2$, melting at 36° and boiling at 265°, occurs in beechwood creosote (B. **12**, 1371). *Methyl*-[3,4,5]-*pyrogallol*-[4,5]-*dimethyl Ether*, *Iridol*, melting at 57° and boiling at 249°, is formed on distilling *iridic acid*, $CO_2H . CH_2 . C_6H_2(OH)(OCH_3)_2$ (B. **26**, 2018).

Propylpyrogallol-dimethyl Ether, Picamar, $C_3H_7 . C_6H_2(OH)(OCH_3)_2$, boiling at 245°, was discovered in beechwood creosote by Reichenbach (B. **11**, 329).

Phloroglucin, $C_6H_3[1,3,5](OH)_3$, melts at 218° when it is rapidly heated. Hlasiwetz first obtained it (1855) in the decomposition of *phloretine* (see this). It can also be prepared from *quercetine, hesperidine*, and other *glucosides* (see these). It is formed from different resins (catechu, kino, dragon's blood, and others), on fusion with caustic potash. It is most easily made by fusing resorcinol with caustic soda (B. **14**, 954; **18**, 1323); by the fusion of orcin and benzene trisulphonic acid with sodium hydroxide; also by the saponification and decomposition of synthetically prepared phloroglucin-tricarboxylic ester, which gives up $3CO_2$ (B. **18**, 3454).

It crystallizes in large, colorless prisms with $2H_2O$; these effloresce in the air. It loses all its water of crystallization at 110°, melts at 218°, and sublimes without decomposition. It has a sweetish taste, and dissolves readily in water, alcohol, and ether. Lead acetate does precipitate it; ferric chloride colors its solution a *dark violet*.

Chlorine oxidizes phloroglucin to dichloracetic acid and tetrachloracetone (p. 46). One of the first intermediate products is *hexachlor-triketo-R-hexylene* (p. 46). For the action of bromine see B. **23**, 1706. It is converted by reduction into *phloroglucite* or sym.-*trioxyhexamethylene* (B. **27**, 357).

Phloroglucin, in most of its reactions,—for example, with phenyl-cyanate (see B. **23**, 269),—conducts itself like a trihydric phenol, $C_6H_3(OH)_3$; on the other hand it unites with three molecules of hydroxylamine to form a *trioxime* (see below), hence it may be considered a triketone—[1,3,5]-*triketo-hexamethylene* (B. **19**, 159):

$$CH\begin{matrix} \diagup C(OH)-CH \diagdown \\ \diagdown C(OH)-CH \diagup \end{matrix}C.OH \quad \text{and} \quad CH_2\begin{matrix} \diagup CO.CH_2 \diagdown \\ \diagdown CO.CH_2 \diagup \end{matrix}CO$$

Trioxybenzene   Triketohexamethylene.

In order to explain the trioxime formation it might be assumed that the [1,3,5]-trioxybenzene formula is the unstable pseudo-form (I, 54) of phloroglucin. This assumption is, however, not necessary. It might be imagined, too, that hydroxylamine first attaches itself to the double union of the trioxybenzene ring, and then the splitting of the three molecules of water took place.

Normal Phloroglucin Ethers.—The *trimethyl ether*, melting at 52° and boiling at 255°, and the *triethyl ether*, melting at 43°, are formed upon heating the alcoholic solutions of phloroglucin with HCl, and then with methyl iodide and caustic potash (B. **21**, 603). The trimethyl ether also results from the action of caustic potash upon *methyl hydrocotoïne* (B. **26**, 784). *Phloroglucintriacetate* melts at 105°. See B. **28**, 24; **29**, R. 990, for the action of phloroglucin upon the sugars. *Nitrosophloroglucindiethyl Ethers: diethoxyquinoxime*, $C_6H_2(OC_2H_5)_2(NO)(OH)$, α-body melting at 117°, β-variety at 192–195° with decomposition—see B. **29**, R. 849. *Trinitrosophloroglucin*, $C_6(NO)_3(OH)_3$ (B. **11**, 1375). *Trinitrophloroglucin*, $C_6(NO_2)_3(OH)_3$. *Triamidophloroglucin*, $C_6(NH_2)_3(OH)_3$, yields *croconic acid* when boiled with MnO_2 and soda (B. **26**, 2185).

When phloroglucin is treated with methyl iodide and alcoholic potash the final product is *Hexamethylphloroglucin* or *hexamethyltriketohexamethylene*, $C_6(CH_3)_6O_3$, melting at 80° and boiling at 248°. Fuming hydrochloric acid decomposes it into di-isopropyl ketone and isobutyric acid (B. **23**, R. 462).

Phloroglucin Trioxime, $C_6H_6(NOH)_3$, is a crystalline powder exploding at 155°. Phenyl hydrazine adds itself to phloroglucin just as it does to oxalo-acetic ester and dioxysuccinic ester (p. 123).

Oxyhydroquinones result from the reduction of oxyquinones.

Oxyhydroquinone, $C_6H_3[1,2,4](OH)_3$, is produced on fusing hydroquinone with KOH (together with tetra- and hexaoxy-diphenyl (B. **18**, R. 24). It is crystalline, very soluble in water and ether, and in aqueous solution soon acquires a dark color. It melts at 140.5°. Ferric chloride colors it a dark greenish-brown. Its **tri-ethyl ether**, $C_6H_3(O.C_2H_5)_3$, is obtained from trioxyethyl benzoic acid (from æsculetin). It can also

be prepared by ethylating ethoxy-hydroquinone. It melts at 34° (B. **20**, 1133). The **trimethyl ether**, $C_6H_3(O.CH_3)_3$, from methoxy-quinone (p. 170), boils at 247°.

TETRAHYDRIC PHENOLS.

There are three possible isomerides; the symmetrical and unsymmetrical varieties are known in a free state, while the third member has been liberated in the form of simple ethers from various plant substances.

(1) **Apionol**, v-*Tetraoxybenzene*, [*Phentetrol*], has been obtained as **Dimethyl Apionol**, $C_6H_2[1,2,3,4](O.CH_3)_2(OH)_2$, by heating apiolic acid with caustic potash. It melts at 106° and boils at 298°. **Tetramethyl Apionol**, $C_6H_2(O.CH_3)_4$, melts at 81°. [1,2]-**Methylene-3,4-dimethyl Apionol**, $C_6H_2(O_2:CH_2)(O.CH_3)_2$, **Apione**, is formed when apiolic acid is heated with dilute sulphuric acid. It melts at 69° (B. **24**, 2608; **29**, 1806).

1-n-*Propyl*-2,3,4,5-*tetraoxybenzene* is obtained as methylene dimethyl ether, dihydroapiol, melting at 25° and boiling at 292°, in the reduction of *isapiol*.

(2) Unsym.-*Tetraoxybenzene*, $C_6H_2[1,2,3,5](OH)_4$, is an amorphous, glassy mass obtained from iretol by the action of hydrochloric acid at 150°. The 1,3-*dimethyl ether* is prepared by reducing 1,3-dimethoxy-2,5-quinone. It melts at 158°. The *tetramethyl ether* melts at 47° and boils at 271° (B. **23**, 2291).

Iretol, $CH_3O.C_6H_2(OH)_3$, melting at 186°, is one of its monomethyl ethers. It is formed together with iridic acid on fusing *irigenin* with potash (B. **26**, 2015).

(3) Symmetrical **Tetraoxy-benzene**, $C_6H_2[1,2,4,5](OH)_4$, is obtained by reducing 1,4-dioxy-2,5-quinone with stannous chloride. It melts at 215–220°. Its *tetra-acetyl-ester* melts at 217° (B. **21**, 3374).

Dichlortetraoxy-benzene, hydrochloranilic acid, $C_6Cl_2(OH)_4$, results in the reduction of chloranilic acid (p. 170) with sulphurous acid (A. **146**, 32).

Amido-s-*Tetraoxybenzene* results from the action of stannous chloride upon nitrodioxyquinone, and also *Nitroamido*-s-*tetra-oxybenzene* and **Diamido-s-tetraoxy-benzene** (B. **18**, 502), by the reduction of nitranilic acid. *Croconic acid* (p. 171) and ammonia are produced on boiling the diamido-body with potash; oxidizing agents convert it into *diamido-dioxy-quinone*.

Hydroeuthiochronic alkali salts—see euthiochronic acid, p. 170.

Pentahydric Phenols are not known. Quercite, which will be discussed in connection with the cyclohexane derivatives, is *pentoxyhexahydrobenzene*.

Hexahydric Phenols.—In describing the benzene-ring formations (p. 42) mention was made of the remarkable isolation of *potassium hexaoxybenzene* or *potassium carbon monoxide* (discovered by Liebig in 1834), which results upon conducting carbon monoxide over heated potassium (confirmed by Nietzki and Benkiser in 1885). Dilute hydrochloric acid, acting upon the fresh mass, yields hexaoxybenzene.

Hexaoxybenzene, $C_6(OH)_6$, is obtained from triquinoyl (p. 171) by reduction with stannous chloride and hydrochloric acid. It separates in the form of small, grayish-white needles, which acquire a reddish-violet color on exposure to the air. They are not fusible, but decompose at about 200°. Concentrated nitric acid oxidizes it to triquinoyl.

It forms the **hexacetyl derivative**, $C_6(O.C_2H_3O)_6$, when heated with acetic acid and sodium acetate. It is a crystalline mass, melting at 203° (B. **18**, 506).

8. QUINONES.

This is the designation ascribed to all derivatives of benzene in which 2H-atoms are replaced by 2O-atoms. The replacement is either in the o- or the p-position. We distinguish ortho-quinones and para-quinones. The latter are especially characteristic of the mono-nucleus aromatic hydrocarbons. Metaquinones are not known.

ORTHOQUINONES.

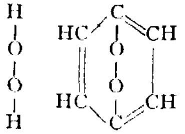
In this series belong the tetrahaloid substitution products of o-benzoquinone, not known in the free condition: *Tetrachlor-o-benzoquinone*, $C_6Cl_4[1,2]O_2$, melting at 131°, and *Tetrabrom-o-benzoquinone*, $C_6Br_4[1,2]O_2$, melting at 150°. They are produced when chlorine or bromine acts upon pyrocatechin dissolved in glacial acetic acid (Zincke, B. **20**, 1776).

Homologous orthoquinones are produced by the action of chlorine upon the corresponding orthodiamine hydrochlorides. The o-diketochlorides are the first products, but they can be reduced to chlorinated o-dioxybenzenes, which yield the chlorinated o-quinones upon oxidation (B. **27**, 560).

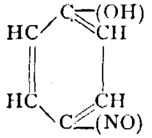
PARAQUINONES.

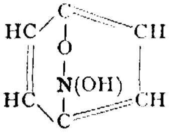
The constitution of the *true quinones* or *paraquinones* of the aromatic hydrocarbons having one nucleus is not fully established. They are considered either as benzene derivatives, the oxygen atoms being assumed to be linked to one another, or as p-dihydrobenzene derivatives, containing two ketone-groups.

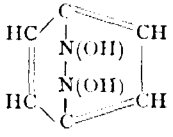
The first view compares the paraquinones to peroxides; they are indeed powerful oxidizing agents. Upon reduction they do not become the p-diglycols of the p-dihydrobenzenes, but p-dioxybenzenes, so-called hydroquinones, which are true benzene derivatives. Further, each oxygen atom, by the action of PCl_5, is replaced by *one* chlorine atom. In opposition to the peroxide formula of the paraquinones we have the p-diketone formula, in support of which we can bring forward the formation of a monoxime and a dioxime, as well as the absorption of 2Br and 4Br by paraquinone (J. pr. Ch. [2] **42**, 61; B. **23**, 3141). Nitrosophenol is considered by most chemists to be quinone-monoxime. Phenylhydrazones of the p-quinones have not been obtained, because the latter bodies oxidize phenylhydrazine (p. 173). The various formulas for ordinary quinone and its oximes are:

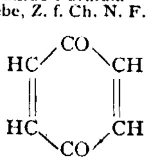


Peroxide Formula
(1867, Graebe, Z. f. Ch. N. F. 3, 39).

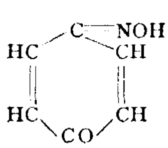




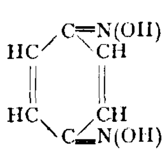




Ketone Formula
(Fittig, A. 180, 23)



Quinone-monoxime
Nitrosophenol



Quinone-dioxime.

Quinone, *Benzoquinone*, $C_6H_4O_2$, melting at 116°, was first obtained in 1838 by Woskresensky upon oxidizing quinic acid, a hexahydrotetraoxybenzoic acid, with manganese peroxide and sulphuric acid. Woskresensky named the new body *Quinoyl*, while Berzelius (Berz. Jahresb. **19**, 407) proposed the name Quinone.

Quinone is made from hydroquinone or p-dioxybenzene (p. 162) by

the action of ferric chloride, and from many p-diderivatives of benzene by oxidation, mostly with potassium bichromate and sulphuric acid; thus, from p-phenylenediamine, sulphanilic acid, p-amidoazobenzene, p-amidophenol, p-phenolsulphonic acid, p-diamidodiphenyl, or benzidine. It is usually prepared by oxidizing aniline with sodium bichromate and sulphuric acid (Nietzki, B. **20**, 2283). It has also been obtained by oxidizing *quinite* (see this).

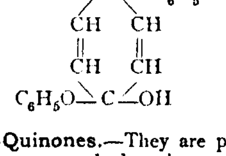
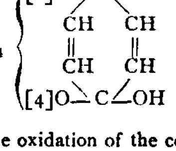
Quinone crystallizes in golden-yellow prisms. It possesses a peculiar, penetrating odor. It attacks the skin. It distils readily with steam, and dissolves easily in hot water, alcohol, and ether. It turns brown on exposure to sunlight. In the presence of the latter it combines to *dioxybenzophenones* with benzaldehyde (1, 75). Reducing agents (SO_2, Zn, and HCl) convert it first into quinhydrone, an addition-product of quinone and hydroquinone, which nascent hydrogen changes into hydroquinone.

Other phenols readily add themselves to quinone (below). Concentrated nitric acid dissolves it in the cold, but when the acid is hot it is decomposed, oxalic and prussic acids being formed. Bromine converts quinone into quinone di- and tetrabromides, melting at 80° and at 170–175°. p-*Diketohexamethylene*, the hydride corresponding to quinone tetrabromide, has been obtained by starting with succino-succinic ester.

Phosphorus pentachloride converts quinone into p-dichlorbenzene (p. 59), hydroxylamine chloride changes it to *quinone-oxime* or *nitrosophenol* (p. 152), and *quinone-dioxime*. Phenylhydrazine reduces it to hydroquinone; α-alkylphenylhydrazines show a similar reducing power, changing simultaneously with tetrazones (p. 131). α-Acidylphenylhydrazines, on the other hand, yield *monohydrazines* of the quinones (p. 172). Aniline combines with quinone, forming *dianilidoquinone*, *dianilidoquinone-anil*, and *dianilidoquinone-dianil*. For the condensations of quinones with acetoacetic ester to form *cumarones*, see the latter.

Quinone Phenol Addition-Products (A. 215, 134).—*Phenoquinone*, $C_6H_4O_2 . 2C_6H_5OH$, melting at 71°, is formed on adding quinone to phenol. It is very volatile. It crystallizes in red needles, which are turned blue by caustic potash, and green by barium hydroxide.

Quinhydrone, $C_6H_4O_2 . C_6H_4(OH)_2$.—This is produced by the direct union of quinone with hydroquinone. It appears as an intermediate product in the reduction of quinone or in the oxidation of hydroquinone,—*e. g.*, in electrolysis (B. **29**, R. 1122),—and is changed by continued oxidation into quinone, and by reduction into hydroquinone. It consists of green prisms or leaflets with metallic lustre, has a quinone-like odor, melts readily, and dissolves in hot water with a brown, in alcohol and ether with a green, color. When it is boiled with water it decomposes into hydroquinone and quinone. The constitution of these compounds probably corresponds to the following formulas (B. **28**, 1615; **29**, R. 903):

Phenoquinone  Quinhydrone C_6H_4 

Homologous p-Quinones.—They are produced (1) by the oxidation of the corresponding p-dioxybenzenes or hydroquinones (even with ferric chloride), of the corresponding p-diamines, p-amidophenols, such as amidothymol and many other disubstitution-products belonging to the p- series, with ferric chloride, chromic acid, and manganese dioxide and sulphuric acid. (2) Even mono-substituted alkyl benzenes yield p-quinones, especially when they are oxidized with chromic acid: This is particularly true of amido- and oxyalkyl benzenes or alkyl phenols. Thus, o-toluidine yields *toluquinone*, while

thymol and carvacrol yield *thymoquinone*, or thymoïl. Frequently an alkyl-group will be displaced, favoring the p-quinone formation, and be substituted by oxygen—*e. g.*, in the oxidation of amidomesitylene (B. **18**, 1150)—to m-*xyloquinone* and of pseudocumidine to p-xyloquinone. (3) p-*Xyloquinone* and *duroquinone* have been synthesized by the action of caustic potash upon the aliphatic α-diketones—*diacetyl* and *acetyl propionyl* (I, 322; II, 42). In this reaction *quinogens* are first produced, afterward follow the p-quinones:

$CH_3.CO.CO.CH_3$ $CH_3.CO.CO.CH_3$	⟶	$CH_3.C(OH).CO.CH_3$ $\vert$ $CH_2—CO.CO.CH_3$	⟶	$CH_3C\ \ .CO.CH$ $\Vert\ \ \ \ \ \ \ \ \ \Vert$ $CH.CO.C.CH_3$
Diacetyl		Dimethylquinogen		p-Xyloquinone.

p-*Xyloquinone* or *phlorone* occurs in the tar of beechwood.

Properties.—The homologous p-quinones are very similar to their prototype—benzoquinone. They are also yellow-colored, possess an odor similar to that of quinone, sublime readily, and behave chemically like p-benzoquinone. They form quinhydrones (p. 168), are easily reduced by sulphurous acid to p-hydroquinones (p. 162), and combine to nitrosophenols (p. 152) and quinone-dioximes (p. 172) with hydroxylamine.

		M. P.	
Toluquinone, ...	$CH_3[1]C_6H_3[2,5]O_2$	67°	
o-**Xyloquinone**, ...	$(CH_3)_2[1,2]C_6H_2[3,6]O_2$	55°	
m-**Xyloquinone**, ...	$(CH_3)_2[1,3]C_6H_2[2,5]O_2$	102°	
p-**Xyloquinone**, ...	$(CH_3)_2[1,4]C_6H_2[2,5]O_2$	123°	
o-**Ethylbenzoquinone**, . . .	$(C_2H_5)[2]C_6H_3[1,4]O_2$	38°	(B. **28**, R. 471).
Pseudocumoquinone, . .	$(CH_3)_3[1,2,4]C_6H[3,6]O_2$	11°	(B. **27**, 1430).
Duroquinone, ...	$(CH_3)_4[1,2,4,5]C_6[3,6]O_2$	111°	(B. **29**, 2171).
Thymoquinone, ...	$(CH_3)(C_3H_7)[1,4]C_6H_2[2,5]O_2$	45°,	B. P., 232°.

When an ethereal solution of thymoquinone is allowed to stand in sunlight for some time, *polythymoquinone*, melting at 200°, separates (B. **18**, 3195). See B. **29**, 2176 for *diduroquinone*.

Quinone Haloids are obtained by the substitution of quinones or by the oxidation of substituted hydroquinones (p. 162).

A mixture of *tri-* and *tetrachlorquinone*, called **chloranil**, consists of bright-yellow leaflets. It is obtained from many benzene compounds (aniline, phenol, isatin) by the action of chlorine or potassium chlorate and hydrochloric acid (B. **29**, R. 236). It oxidizes and serves as an oxidizing agent in the manufacture of coloring-matters.

Trichlor- and tetrachlorquinone are separated from one another by the insolubility of the latter in water. The chlorquinones are obtained from chlorhydroquinones by oxidation with nitric acid (A. **146**, 9; **210**, 145; **234**, 14):

	M. P.		M. P.
Monochlorquinone, . . .	57°;	**Monobromquinone**, ...	55°.
[2,5]-**Dichlorquinone**, ...	159°;	[2,5]-**Dibromquinone**, ...	188°.
[2,6]-**Dichlorquinone**, ...	120°;	[2,6]-**Dibromquinone**, ...	122°.
Trichlorquinone, ...	166°;	**Tribromquinone**, ...	147°.
Tetrachlorquinone sublimes.		**Tetrabromquinone** sublimes.	

PCl_5 converts tetrachlorquinone into phosphorus-containing derivatives, $C_6Cl_5.OPOCl_2$ (?), and then into hexachlorbenzene (p. 59) (B. **24**, 927). It absorbs two atoms of chlorine and becomes *hexachlor*-p-*diketo*-R-*hexene* (p. 45), which caustic soda resolves into dichlormaleïc acid and trichlorethylene. Potassium hydroxide converts trichlorquinone and tetrachlorquinone into potassium chloranilate (p. 170), and tribrom- and tetrabromquinone into potassium bromanilate.

Nitroquinone, $NO_2C_6H_3O_2$, decomposing at 206°, consists of yellow glistening crystals, and is formed by oxidizing 2-nitro-p-amidophenol, $NO_2[2]C_6H_3[4]NH_2[1]OH$, with potassium dichromate and sulphuric acid. It is very sparingly soluble in water, not volatile with aqueous vapor, and dissolves with difficulty in ether, and very readily in alcohol and in chloroform. It imparts a black color to the skin (B. **28**, 1386).

Amidoquinones.—*Chloranilamide*, $C_6Cl_2(NH_2)_2O_2$, is obtained from chloranilic acid. Aniline, acting upon a hot alcoholic solution of quinone, produces not only hydroquinone, but also *dianilidoquinone*, *dianilidoquinone-anil*, and *-dianil* (p. 173), as well as 2,5-dioxy-1,4-quinone (below).

OXYQUINONES AND POLYQUINOYLS.

Benzene Oxyquinones.—Methoxyquinone, $CH_3O[2]C_6H_3:O_2$, melting at 140°, is produced by oxidizing o-amidoanisol, $C_6H_4(NH_2).O.CH_3$, with chromic acid.

Chloranilamic Acid, $C_6Cl_2(NH_2)(OH)O_2$, is obtained from chloranil.

2,6-*Dimethoxyquinone*, $(CH_3O)_2[2,6]C_6H_2O_2$, melting at 249°, results from the oxidation of trimethylpyrogallol and trimethylphloroglucin (p. 165) (B. **26**, 784).

2,5 *Dioxyquinone*, $(HO)_2[2.5]C_6H_2O_2$, is obtained from dioxyquinone dicarboxylic acid (see this) by boiling with hydrochloric acid, by the oxidation of diamido-resorcin (B. **21**, 2374; **22**, 1285), and by the action of dilute sulphuric acid upon dianilidoquinone (B. **23**, 904). It separates in small blackish-brown crystals, which sublime above 185°. Stannous chloride reduces it to symmetrical tetraoxybenzene (p. 166), and dianilidoquinone is produced when it is heated with aniline. Substitution-products of 2,5-dioxyquinone have been obtained from tetrachlor- and tetrabromquinone as starting-out substances. Two of their halogen atoms are exchanged with extreme ease.

Chloranilic Acid, $C_6Cl_2(OH)_2O_2$, reddish, shining scales, is separated by acids from *potassium chloranilate*, $C_6Cl_2(OK)_2O_2 + H_2O$, which crystallizes in dark-red needles, dissolving with difficulty in water. Potassium chloranilate is produced as well from *tri-* as from *tetrachlorquinone* by the action of caustic potash. Hypochlorous acid or chlorine acting upon chloranilic acid, produces *tri-* or *tetrachlortetraketohexamethylene*, which change quite readily with the intermediate production of unstable oxyacids into *trichlor-* and *tetrachlortriketopentamethylene* (B. **25**, 827, 842).

Bromanilic Acid, $C_6Br_2(OH)_2O_2$, corresponds to chloranilic acid and with bromine yields similar transposition-products to those obtained from it by the action of chlorine.

Nitranilic Acid, $C_6(NO_2)_2O_2(OH)_2$.—It crystallizes with water in golden-yellow needles or plates, melts in its water of crystallization, becomes anhydrous at 100°, and detonates at 170° without melting. It is formed from quinone and hydroquinone with nitrous acid, and from terephthalic and dioxyquinone-terephthalic acids by the action of fuming nitric acid. When nitroanilic acid is reduced, it yields diamidotetraoxybenzene (p. 166), which renders possible the transition from chloranil to triquinoyl (see below), and potassium hexaoxybenzene.

Amidoanilic Acid, Diamidodioxyquinone, $C_6(NH_2)_2(OH)_2O_2$, reddish-blue needles, formed from diamidotetraoxybenzene by oxidation in the air or by nitrous acid.

Potassium Euthiochronate, $C_6(SO_3K)_2(OH)_2O_2$, see dichlorhydroquinone-disulphonic acid (p. 164).

Tetraoxyquinone, $C_6(O_2)(OH)_4$, formerly called dihydrocarboxylic acid, is obtained by oxidizing the aqueous solution of hexaoxybenzene by exposure to the air (B. **18**, 507, 1837). It may also be obtained from diamido-dioxyquinone by boiling with hydrochloric acid, as well as by the action of concentrated nitric acid upon inosite. Metallic black needles, with a green, metallic reflex. It is a strong dibasic acid.

Homologous Oxyquinones result upon treating haloid quinone homologues with caustic potash, and on heating amido- or anilidoquinones with alcoholic hydrochloric acid or sulphuric acid. *Dianilidotoluquinone*, melting at 232°, yields anilido-oxytoluquinone, decomposing at 250°, and dioxytoluquinone, $CH_3.C_6H(OH)_2O_2$, melting at 177° (B. **16**, 1559). *Oxythymoquinone*, $(C_3H_7)(CH_3)C_6H(OH):O_2$, melting at 166°, is obtained from brom- or methylamidothymoquinone. *Dioxythymoquinone* melts at 213° (B. **14**, 95).

It is also very probable that *pipitzahoïc acid*, $C_{15}H_{19}(OH):O_2$, found in the root of *Trixis pipitzahuac* and melting at 103°, belongs to the oxyquinones, containing but one nucleus. It recalls, by its behavior, oxythymoquinone. *Oxypipitzahoïc Acid*, C_9H_{18}:-$C_6(OH)_2:O_2$ (?), melts at 138° (A. **237**, 90).

Polyquinoyl Compounds.—As mentioned under benzoquinone (p. 167), Woskresensky originally called this compound *quinoyl*. Nietzki and Benckiser introduced this

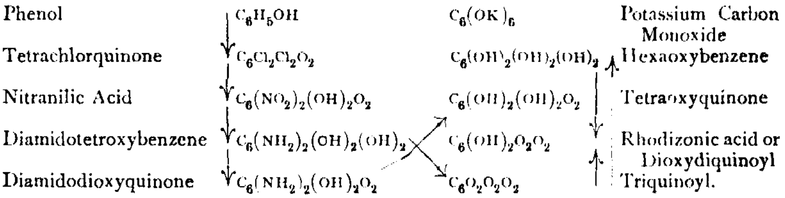
name in a different sense. They applied it to the quinone-group O_2, when they discovered dioxydiquinoylbenzene and triquinoylbenzene to be bodies containing more than one quinone-group O_2. For simplicity's sake they abridged these names to *dioxydiquinoyl* and *triquinoyl*.

Dioxydiquinoyl, $C_6(O_2)(O_2)(OH)_2$, called *rhodizonic* acid, is prepared by reducing triquinoyl with aqueous sulphurous acid (B. **18**, 513). It consists of colorless leaflets, very readily soluble in water. It decomposes quite rapidly in aqueous solution. The *potassium salt*, $C_6O_4(OK)_2$, may be obtained by treating the acid with potashes, and also by washing potassium-hexaoxybenzene (potassium carbon monoxide, p. 166) with alcohol. It forms dark blue needles, dissolving in water with an intense yellow color (B. **18**, 1838).

Consult B. **23**, 3140, for the constitution of rhodizonic acid.

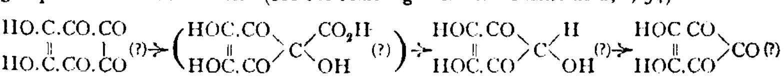
Triquinoyl, $C_6O_6 + 8H_2O$, is probably hexaketo-hexamethylene (B. **20**, 322). It results upon oxidizing dioxydiquinoyl and diamidotetraoxybenzene (p. 166) with nitric acid. It is a white, micro-crystalline powder (B. **18**, 504). It melts about 95°, giving up water and CO_2. It is likewise decomposed by warming it with water to 90°. Stannous chloride reduces it to hexaoxybenzene, which is oxidized in alkaline solution to tetraoxyquinone, $C_6(O_2)(OH)_4$ (see above).

Nietzki and Benckiser (1885) discovered the relations existing between potassium carbon monoxide and phenol. Compare the following:



Addendum.—Pentacarbocyclic compounds are readily formed from triquinoyl and dioxydiquinoyl, as well as from some hexa-substitution derivatives of benzene, from which these polyquinoyl bodies arise—*e. g.*, hexaoxybenzene, diamidotetraoxybenzene, etc. They will accordingly be discussed after the polyquinoyls (pp. 25, 26).

Croconic Acid Hydride, $C_5H_4O_5$, is formed upon treating rhodizonic acid with excessive alkali, or croconic acid with hydriodic acid. It is distinguished by its *barium salt*, $C_5H_2BaO_5 + 2H_2O$. Its formation is probably due to the breaking down of an unstable oxyacid, produced by the action of the caustic alkali upon two of the combined CO-groups of the rhodizonic acid (see the rearrangement of benzilic acid, I, 54):



Rhodizonic Acid (B. **23**, 3140) | Unstable Oxyacid | Croconic Acid Hydride | Croconic Acid.

Croconic Acid, $C_5O_3(OH)_2 + 3H_2O$, consists of sulphur-yellow leaflets; it loses its water of crystallization at 100°. It dissolves very readily in water and alcohol, and is produced by the alkaline oxidation of most of the hexa-substituted benzene-derivatives—*e. g.*, hexaoxybenzene, dioxydiquinoyl, diamidotetraoxybenzene, etc. The hydride of croconic acid is an intermediate product, which changes quite readily to the acid. Triquinoyl, when boiled with water, decomposes into carbon dioxide and croconic acid:

$$C_6O_6 + H_2O = C_5H_2O_5 + CO_2.$$

Its *potassium salt*, $C_5O_5K_2 + 3H_2O$, crystallizes in orange-yellow needles; hence the name from κρόκος, safran (Gmelin, 1825). When oxidized with nitric acid or chlorine the product is—

Leuconic Acid, $C_5O_5 + 4H_2O$, Pentaketocyclopentane, which is reconverted into croconic acid by sulphur dioxide. This acid bears the same relation to croconic acid

that rhodizonic acid sustains to triquinoyl. It is very soluble in water, but dissolves with difficulty in alcohol and ether. It crystallizes in small colorless needles. The **penta-oxime**, $C_5(:N.OH)_5$, decomposing at 172°, is isomeric with fulminic acid, cyanic acid, cyanuric acid, and by reduction yields **penta-amido-pentol**, $C_5H(NH_2)_5$, **penta-amido-cyclopentadiēn** (see p. 25) (B. **22**, 916).

QUINONE NITROGEN DERIVATIVES.

The quinone oxygen atoms can be replaced by N(OH), NCl, NH, NC_6H_5, and similar groups.

Quinone Dioximes.—In connection with the p-nitrosophenols (p. 152), and in the explanation of Fittig's diketone formula for p-quinone, it was indicated that many chemists regarded the p-nitrosophenols, resulting from the action of hydroxylamine hydrochloride upon the p-quinones, as *monoximes* of the latter. Indeed, the p-nitrosophenols, by action of hydroxylamine hydrochloride, change to p *quinonedioximes*. It is true these two classes can be viewed as constituted according to the peroxide formula of the p-quinones. Their dioximes unite with acetic anhydride to diacetyl compounds. p-Dinitrosobenzenes are produced by the oxidation of their alkaline solutions (also on exposure to the air). Nitric acid oxidizes them to p-dinitrobenzenes (B. **21**, 428).

p-*Quinone Dioxime*, $C_6H_4(N.OH)_2$, consists of colorless or yellow needles, which decompose at 240°. *Toluquinone Dioxime* explodes at 220° (B. **21**, 679). p-*Xyloquinone Dioxime* melts about 272° (B. **20**, 978). Dinitroresorcinol and hydroxylamine yield *diquinoyltrioxime*, $C_6H_2O(NOH)_3$, and *diquinoyltetroxime*, $C_6H_2(NOH)_4$ (B. **30**, 181).

Quinone-chlorimides.—We must regard them either as diketones or peroxides, in which oxygen is replaced by the group NCl. The latter view corresponds to the formulas:

$$C_6H_4\begin{cases}O\\NCl\end{cases} \text{ or } C_6H_4\begin{cases}O\\|\\NCl\end{cases} \quad\text{and}\quad C_6H_4\begin{cases}NCl\\NCl\end{cases} \text{ or } C_6H_4\begin{cases}NCl\\|\\NCl\end{cases}$$

Quinone Chlorimide — Quinone Dichlorimide.

They are produced from p-amidophenols and p-phenylenediamines (their HCl-salts) by oxidation with an aqueous solution of bleaching lime. They revert to p-amidophenols or p-phenylenediamines upon reduction. The monochlorimides form the indophenol dyestuffs (p. 173) with phenols and tertiary anilines.

Quinone-chlorimide, $O[1]C_6H_4[4]NCl$, forms golden-yellow crystals, which melt at 85°, volatilize readily with steam and smell like quinone. It is easily soluble in hot water, alcohol, and ether. When boiled with water it decomposes into NH_4Cl and quinone (J. pr. Ch. [2] **23**, 435).

Quinone-dichlorimide, $C_6H_4[1,4](N_2Cl_2)$, crystallizes in needles which deflagrate at 124° (B. **12**, 47).

Trichlor-quinone-chlorimide melts at 118° (J. pr. Ch. [2] **24**, 429).

Dibrom-quinone-chlorimide melts at 80° (B. **16**, 2845).

Quinone Phenylhydrazones.—While phenylhydrazine and alkylic phenylhydrazines are oxidized by quinone, α-benzoylphenylhydrazine and quinone yield *Quinone-benzoylphenylhydrazone*, $C_6H_4(O):NN(CO.C_6H_5)C_6H_5$, melting at 171°. Alkali or sulphuric acid readily decomposes it into benzoic acid and p-oxyazobenzene, which yields the isomeric p-benzoxyazobenzene, $C_6H_5CO.OC_6H_4N_2C_6H_5$, upon introducing the benzoyl group. The o-*azophenols* are very probably hydrazones of o-quinones (p. 156 and B. **28**, 2415).

Quinone-imides.—*Quinoanils: Diamidoquinone-imide*, $(NH_2)_2C_6H_2(O)(NH)$, or *amidodiimidophenol*, $(HO)(NH_2)C_6H_2(NH)_2$, is made from triamidophenol (A. **215**, 351).

Quinone Phenylimide, Quinone Monanil, $C_6H_4\begin{cases}O\\|\\NC_6H_5\end{cases}$ or $C_6H_4\begin{cases}O\\N.C_6H_5\end{cases}$ melting at 97°, consists of fiery-red crystals. It is formed upon oxidizing p-oxydiphenylamine in benzene solution with mercuric oxide, and upon reduction reverts to the same (B. **21**, R. 434).

Diphenyl-p-*azophenylene*, *Quinone Dianil*, $C_6H_4<\begin{matrix}N.C_6H_5\\|\\N.C_6H_5\end{matrix}$ or $C_6H_4\lessgtr\begin{matrix}N.C_6H_5\\N.C_6H_5\end{matrix}$, melting at 176°–180°, results from the oxidation of diphenylamine (p. 80), and diphenyl-p-phenylenediamine (B. **21**, R. 656). Reduction converts quinonedianil into diphenyl-p-phenylenediamine. Both anils sustain the same relation to the corresponding diphenylamine-derivatives that quinone bears to hydroquinone:

$$C_6H_4<\begin{matrix}O\\|\\O\end{matrix} \qquad C_6H_4<\begin{matrix}O\\|\\NC_6H_5\end{matrix} \qquad C_6H_4<\begin{matrix}NC_6H_5\\|\\NC_6H_5\end{matrix}$$

$$C_6H_4<\begin{matrix}OH\\OH\end{matrix} \qquad C_6H_4<\begin{matrix}OH\\NHC_6H_5\end{matrix} \qquad C_6H_4<\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix}.$$

Two phenylamido-groups can be as readily introduced into the benzene residue of quinone-anil and quinone-dianil as into quinone itself, from which, on boiling its alcoholic solution with aniline, *dianilidoquinone* (together with hydroquinone) results. In the presence of acetic acid the product is *dianilidoquinone-anil*, $(C_6H_5NH)_2C_6H_2(O)(NC_6H_5)$, melting at 202°; brown-red needles. It is also formed upon digesting quinone-monanil (together with p-oxydiphenylamine, B. **21**, R. 656) with aniline, and when aniline is oxidized with hydrogen peroxide in a feebly acid solution (B. **25**, 3574).

Dianilidoquinone-dianil, *Azophenine*, $(C_6H_5NH)_2C_6H_2(NC_6H_5)_2$, melting at 241°, consists of garnet-red leaflets. It is produced (1) by digesting quinone-dianil with aniline (diphenyl-p-phenylenediamine is formed at the same time, B. **21**, R. 656); (2) by fusing quinone with aniline and aniline hydrochloride (B. **21**, R. 683); (3) by the action of aniline upon amidoazobenzene, p-nitrosophenol, and p-nitrosodiphenylamine (B. **20**, 2480). It changes to *fluorindin* when heated (B. **23**, 2791).

The quinone-anils are important intermediate products in the formation of the *induline* dyes (see these) (B. **25**, 2731; A. **262**, 247).

Indophenols and **Indoanilines.**—These compounds are obtained from quinone-monoanil or quinone-phenylimide by replacing the p-hydrogen atom of the anil-group by an OH- or an NH_2-group. They are dyes. Like many members of this class, they are decolorized by the addition of hydrogen. The resulting bodies are leuco-compounds, p-disubstituted diphenylamines. (Nomenclature, B. **29**, R. 94.)

Indophenols are produced (1) by allowing the quinone-chlorimides to act upon phenols; (2) by oxidizing a mixture of a p-amidophenol and phenol. They dissolve in alcohol with a red color, and possess a phenol-like character. Their salts with the alkalies and ammonia dissolve in water with a *blue* color.

Quinone-phenolimide, $C_6H_4<\begin{matrix}N.C_6H_4OH\\|\\O\end{matrix}$, also results upon heating phenol-blue with soda-lye (B. **18**, 2916), but owing to its instability, cannot be obtained in a free condition. By reduction it changes to colorless p-dioxydiphenylamine. **Dibromquinone-phenolimide**, $C_6H_2Br_2<\begin{matrix}N.C_6H_4OH\\|\\O\end{matrix}$, from dibromquinone-chlorimide, is more stable than quinone-phenolimide. Free dibromphenolimide crystallizes in dark-red prisms having a metallic lustre; they dissolve in alcohol and ether with a fuchsine-red color. Strong mineral acids decompose it into dibromphenol and quinone.

The **Indoanilines** are produced (1) by the action of quinone chlorimide upon dimethyl aniline in alcoholic solution; (2) by the action of nitroso- and nitro-dimethyl-aniline upon phenol in alkaline solution, especially in the presence of reducing agents (Witt, 1879); (3) by the oxidation in *alkaline* solution (with sodium hypochlorite) of a mixture of a p-phenylenediamine with a phenol, or of a p-amidophenol with a primary monamine.

The indoanilines are feeble bases. They are rather stable toward the alkalies; acids quickly decompose them into quinones and the p-phenylenediamines. They are changed to the leuco-compounds: amido-oxy-diphenylamines, by reduction (absorption of two hydrogen atoms); these dissolve readily in alkalies, and are readily reconverted (oxidized) into indoanilines (by exposure of their alkaline solution to the air). The free indoanilines have a deep-blue color, and can be applied as dyestuffs. For this purpose

they are converted into their alkaline leuco-derivatives, which are soluble, and the material is impregnated or printed with these. Oxidation (by exposure to the air or with $K_2Cr_2O_7$) develops the color. The simplest aniline is **Quinone Anilinimide,** $C_6H_4<\begin{smallmatrix} N . C_6H_4 . NH_2 \\ | \\ O \end{smallmatrix}$, a violet dye, formed by the oxidation of p-phenylene diamine, $C_6H_4(NH_2)_2$, with phenol. **Quinone-dimethyl-anilinimide** (phenol blue), $C_6H_4<\begin{smallmatrix} N . C_6H_4 . N(CH_3)_2 \\ | \\ O \end{smallmatrix}$, results from unsym.-dimethyl-p-phenylenediamine and phenol. It has a greenish blue color and dissolves in acids with a blue color. When boiled with soda-lye it splits off dimethylamine and becomes quinone-phenolimide. Sulphuric acid decomposes it into quinone and dimethyl-p-phenylenediamine. This is a general reaction, hence can be used opportunely for the preparation of quinones (B. 28, R. 471; 29, R. 24).

Indamines.—These are derived from the indoanilines by the replacement of the quinone-oxygen atom by the imido- or alkylimido-group. They are therefore derivatives of the unknown quinone diimide, and bear an intimate relation to p-diamidodiphenylamine, which is formed by the reduction of the simplest indamine and is the leuco-derivative of the latter.

The *Indamines* arise (1) by oxidation, in neutral solution and in the cold, of a mixture of a p-phenylenediamine with an aniline (Nietzki), or (2) by the action of nitrosodimethyl aniline upon anilines or m-diamines (Witt). They are feeble bases, forming blue- or green-colored salts with acids, but with an excess of the latter are very easily split up into quinone and the diamine. Because of their instability they find no application, and are only important as intermediate products in the manufacture of thionine and safranine dyestuffs (into which they can be readily transposed). For the relations of the indophenols, indanilines, and indamines to the dyes of the *oxazine-*, *thiazine-*, and *diazine-series*—*e. g.*, resorufin, methylene blue—the indulines and safranines, see the latter. The simplest indamine is—

Phenylene Blue, $C_6H_4<\begin{smallmatrix} N . C_6H_4NH_2 \\ | \\ NH \end{smallmatrix}$ or $N\begin{smallmatrix} \diagup C_6H_4NH_2 \\ \diagdown C_6H_4 = NH \end{smallmatrix}$. This is produced by the oxidation of p-phenylenediamine with aniline. Its salts are greenish-blue in color. It yields diamido-diphenylamine by reduction. Its tetramethyl-derivative is—

Dimethylphenylene Green, $N<\begin{smallmatrix} C_6H_4 . N(CH_3)_2 \\ C_6H_4 . N(CH_3)_2Cl \end{smallmatrix}$ (Bindschedler's green). This is obtained by oxidizing dimethyl paraphenylenediamine with dimethyl aniline. Its salts dissolve in water with a beautiful green color. Its reduction yields tetramethyl-diamido-diphenylamine. Digestion with dilute acids resolves it into quinone and dimethylamine (B. 16, 865; 17, 223). On standing with soda-lye, dimethylamine splits off and phenol blue is produced; this further separates into quinone phenolimide (p. 173) (B. 18, 2915).

Toluylene Blue, $N<\begin{smallmatrix} C_6H_4 . N(CH_3)_2 \\ C_7H_5(NH_2) . NH \end{smallmatrix}$, results from ordinary toluylene diamine (p. 95) by oxidizing it mixed with dimethyl-p-phenylenediamine, or by the action of HCl-nitroso-dimethylaniline. Its salts with one equivalent of acid are of a beautiful blue color, and are decolorized by an excess of mineral acids with formation of the diacid salts. It is converted into toluylene red (see this) on boiling with water.

The genetic connection of the indamines with the indoanilines and indophenol is shown in the possibility of converting the simplest indamine into quinone aniline imide, and the latter into quinone-phenol-imide (Möhlau, B. 16, 2843; 18, 2915).

Representatives of the indophenols, indoanilines, and indamines, containing the naphthaline residue are also known in great numbers, and many, like *Naphthol Blue* (see this) or "*Indophenol*," have been applied technically (B. 18, 2916).

9. PHENYL-PARAFFIN ALCOHOLS AND THEIR OXIDATION PRODUCTS.

In the preceding sections those classes of aromatic hydrocarbons containing one nucleus were described, which resulted from the substitution of the hydrogen atoms of benzene or the benzene residue of the alkylbenzenes by atoms of other elements or by atomic groups: the ***halogen*** substitution products (pp. 57–63), the *nitrogen-containing* derivatives of the benzene hydrocarbons (p. 63), the aromatic *phosphorus*, *arsenic*, *antimony*, *bismuth*, *boron*, *silicon*, and *tin* derivatives (pp. 131–133), the phenyl *metal* compounds (p. 133), the *sulpho-acids* and their relatives (pp. 133–140), the *phenols* (p. 140), and the *quinones*.

Attached to these are those classes of bodies formed by the replacement of hydrogen atoms in the side-groups of the alkylbenzenes. As in the aliphatic series, the oxygen-containing products are considered the most important. Each class of these derivatives is followed by the corresponding halogen, sulphur, and nitrogen compounds, in which all, or at least a part, of the carbon valences, saturated in the principal compounds by oxygen, are taken up with the elements just named. Prominent among these, as with the aliphatic derivatives, are those bodies in which *one* carbon atom of an alkyl side-chain is combined with oxygen:

(1*a*) *The monohydric phenyl-paraffin alcohols and their oxidation products: aldehydes, ketones, carboxylic acids.*

Naturally these compounds, as far as the reactivity of the aliphatic residue is concerned, manifest great similarity to the monohydric aliphatic alcohols and their oxidation products (I, 109). This is recalled by their nomenclature and the view that they are phenylsubstitution products of aliphatic substances (p. 32).

Each of these alkyl-benzene derivatives constitutes a starting-out substance from which, by the replacement of hydrogen atoms of the phenyl residue, as with benzene itself, numerous derivatives can be deduced. In general the benzene substitution products of the *phenyl fatty* bodies, so far as they are worth mention, will be introduced after the corresponding principal bodies. Only the derivatives of monohydric aromatic alcohols, having hydroxyl in their benzene residue, and their oxidation products, which manifest at the same time a phenol character, will be grouped together as—

(1*b*) *Monohydric oxyphenyl-paraffin alcohols and their oxidation products.*

Then will follow (2) *polyhydric phenyl-paraffin alcohols, in which but one hydroxyl group is joined to a side-chain, and their oxidation products.* The conclusion of this section will be (3) *polyhydric phenyl-paraffin alcohols, in which more than one hydroxyl group is attached to a side-chain, and their oxidation products.*

(1a) MONOHYDRIC PHENYL-PARAFFIN ALCOHOLS AND THEIR OXIDATION PRODUCTS.

1. MONOHYDRIC PHENYL-PARAFFIN ALCOHOLS.

The *true alcohols* of the benzene series are produced by the entrance of an hydroxyl group into the side-chain of an alkylbenzene: *primary, secondary*, and *tertiary*. The primary alcohols, upon oxidation, yield *aldehydes* and *acids*, the secondary change to *ketones*:

↓ Benzyl Alcohol,	$C_6H_5.CH_2.OH$	↓ Phenylmethyl Carbinol,	$C_6H_5CH(OH)CH_3$
↓ Benzaldehyde,	$C_6H_5.CHO$	Acetophenone,	$C_6H_5.CO.CH_3$
Benzoic Acid,	$C_6H_5.COOH$		

Formations.—The similarity of benzyl alcohol and its homologues to ethyl alcohol finds expression at the very outset in the methods of producing both classes: (1) by saponification of alkyl benzenes containing an halogen atom in the side-chain—the haloid acid esters of the benzyl alcohols—*e. g.*, benzyl chloride with water alone (A. **196**, 353), with water and lead oxide (A. **143**, 81), or with potashes. Benzyl alcohols are also produced by converting the chlorides into acetates and saponifying the latter.

(2) By the action of nitrous acid upon primary amines, the reduction products of aromatic acid nitriles—*e. g.*, cumo- and hemimellibenzyl alcohol.

(3) By the action of nascent hydrogen on the corresponding aldehydes and ketones.

(4) By heating the aldehydes, or letting them stand with alcoholic or aqueous potash (B. **14**, 2394), whereby acids are formed at the same time:

$$2C_6H_5.CHO + KOH = C_6H_5.CH_2.OH + C_6H_5.CO_2K.$$

This reaction we do not observe with the monohydric paraffin alcohols.

(5) By reducing amides of aromatic carboxylic acids, containing the carboxyl group attached to the benzene nucleus, with sodium amalgam in acid solution (B. **24**, 173).

(6) By the reduction of unsaturated alcohols: cinnamyl alcohol, $C_6H_5CH = CH.CH_2OH$, becomes hydrocinnamyl alcohol, $C_6H_5.CH_2.CH_2.CH_2OH$ (see allyl alcohol, I, 130).

(7) They are formed in the nucleus-synthetic way when zinc methide acts upon acid chlorides: phenylacetyl chloride and zinc methide yield *benzyl dimethyl carbinol* (1, 114).

Benzyl Alcohol, *Phenyl Carbinol,* [Phenmethylol], $C_6H_5CH_2OH$, boiling at 206°, with sp. gravity 1.062 (0°), is isomeric with the cresols (p. 144). It occurs as benzyl-benzoic ester and benzyl-cinnamic ester in the balsams of Peru and Tolu, and in storax (A. **169**, 289). It is produced by the methods (1), (2), (3), (4), given above, from benzaldehyde, benzyl chloride, and benzamide. Reactions (1) and (3) are used as methods of preparation. It is a colorless liquid, with a faint aromatic odor. It dissolves with difficulty in water, but readily in alcohol and ether. It yields benzaldehyde and benzoic acid when oxidized. Heated with hydrochloric acid or hydrobromic acid, the OH-group is replaced by halogens. Benzoic acid and toluene result on distilling it with concentrated potash.

History.—As early as 1832 Liebig and Wöhler, in the course of their celebrated investigation upon the radical benzoyl, had this alcohol in hand as the result of the interaction of alcoholic potash and benzaldehyde (A. **3**, 254, 261). Cannizzaro (1853) was the first to discover the alcohol in studying this reaction.

Homologous Benzyl Alcohols.—The primary alcohols are chiefly made by methods (1), (2), (3), (4); hydrocinnamyl alcohol by method (6); the secondary alcohols by method (1), or by the reduction of the ketones according to method (3), and the tertiary alcohols, like benzyldimethyl carbinol, by method (7).

Nucleus Homologous Benzyl Alcohols:

		M. P.	B. P.	
o-Tolyl Carbinol, . .	$CH_3[2]C_6H_4[1]CH_2OH$	34°	223°	(B. **24**, 174).
m-Tolyl Carbinol, . .	$CH_3[3]C_6H_4[1]CH_2OH$	liquid	217°	(B. **18**, R. 66).
p-Tolyl Carbinol, . .	$CH_3[4]C_6H_4[1]CH_2 . OH$	59°	217°	(A. **124**, 255).
2,4-Dimethyl Benzyl Alcohol, ...	$(CH_3)_2[2,4]C_6H_3[1]CH_2 . OH$	22°	232°	(B. **21**, 3085).
3,5-Mesityl Alcohol, . .	$(CH_3)_2[3,5]C_6H_3[1]CH_2 . OH$	liquid	220°	(B **16**, 1577).
2,4,5-Cumobenzyl Alcohol,	$(CH_3)_3[2,4,5]C_6H_2[1]CH_2 . OH$	168°	—	(B. **24**, 2411).
3,4,5 Hemimellibenzyl Alcohol, ...	$(CH_3)_3[3,4,5]C_6H_2[1]CH_2 . OH$	78°	—	(B. **24**, 2411).
Mellithyl Alcohol, .	$(CH_3)_5C_6 . CH_2OH$	160°	—	(B **22**, 1217).
p-Cumin Alcohol, . .	$(CH_3)_2CH[4]C_6H_4[1]CH_2 . OH$	—	246°.	

Other homologues are the *phenyl ethyl alcohols*:

Benzyl Carbinol, $C_6H_5CH_2 \, CH_2OH$, boils at 212° (B. **9**, 373).

Phenyl Methyl Carbinol, $C_6H_5 . CH(OH)CH_3$, boils at 203° (B. **7**, 141).

Phenyl Propyl Alcohols: *Hydrocinnamyl Alcohol*, $C_6H_5 . CH_2 . CH_2 . CH_2OH$, boils at 235°. It is obtained from its cinnamic acid ester, which is present in *storax* (A. **188**, 202). *Benzyl Methyl Carbinol*, $C_6H_5 . CH_2 . CH(OH) . CH_3$, boils at 215°. *Phenylethyl Carbinol*, $C_6H_5CH(OH) . CH_2 . CH_3$, boils at 221°. *Benzyldimethyl Carbinol*, $C_6H_5 . CH_2 . C(OH)(CH_3)_2$, melts at 21° and boils at 225°.

Derivatives of the Phenyl-Paraffin Alcohols.—*Haloid Esters.* Benzyl chloride and benzyl bromide are produced when chlorine or bromine (p. 61) acts upon boiling toluene (Beilstein, A. **143**, 369). Benzyl chloride, bromide, and iodide are also formed from benzyl alcohol and the haloid acids, and benzyl iodide by the action of potassium iodide upon benzyl chloride (A. **224**, 126):

Benzyl Chloride, . . .	$C_6H_5 . CH_2Cl$	liquid	B. P. 176°.
Benzyl Bromide, . . .	$C_6H_5 . CH_2Br$	"	" 210°.
Benzyl Iodide, . . .	$C_6H_5 . CH_2I$	melts at 24° and decomposes.	

Benzyl Chloride, isomeric with the three chlortoluenes (p. 61), is an important reagent, by means of which numerous derivatives of benzyl alcohol have been prepared, as its chlorine atom is readily exchanged. It passes into benzyl alcohol when boiled with water. Heated with water and lead nitrate it yields benzaldehyde, and by oxidation benzoic acid:

$$C_6H_5CH_3 \longrightarrow C_6H_5 . CH_2Cl - \left\{ \begin{array}{l} \longrightarrow C_6H_5 . CH_2OH \\ \longrightarrow C_6H_5 . CHO \longrightarrow C_6H_5COOH. \end{array} \right.$$

The following *ethers* have been made by the action of sodium alcoholates upon benzyl chloride: *Benzyl Methyl Ether* boils at 168°. The *ethyl ether* boils at 185°. The *benzyl ether* (A. **241**, 374), $(C_6H_5CH_2)_2O$, boiling at 296°, results from the action of boron trioxide upon benzyl alcohol. *Methylene Dibenzyl Ether*, $CH_2(OCH_2 . C_6H_5)_2$ (A. **240**, 200). *Benzylarabinoside*, $C_5H_9O_5 . CH_2 . C_6H_5$, melts at 172° (B. **27**, 2482). *Benzylphenyl Ether* melts at 39° and boils at 287°.

Homologous Benzyl Chlorides. *α-Chlorethyl Benzene*, $C_6H_5CHCl . CH_3$, boils at 194°. (ω-) *β-Chlorethyl Benzene*, $C_6H_5 . CH_2 . CH_2Cl$, boils at 93° (17 mm.). o-, m-, p-*Methyl Benzyl Chloride*, $CH_3 . C_6H_4CH_2Cl$, boil at 198°, 195°, and 192° respectively. *α-Chlorpropyl Benzene*, $C_6H_5 . CHCl . CH_2 . CH_3$, and *β-Chlorpropyl Benzene*, C_6H_5-

$CH_2CHClCH_3$, boil about 203–207° with the splitting off of hydrochloric acid and the production of *α*-phenylpropylene, $C_6H_5 . CH : CH . CH_3$, and allyl benzene, $C_6H_5CH_2$-$CH = CH_2$.

Benzyl Phosphates: The *mono-* melts at 78°, the *di-* is liquid, and the *tri-* melts at 64° (A. **262**, 211).

Esters of Carbonic Acid. *Benzyl Acetate*, $C_6H_5CH_2 . O . CO . CH_3$, boils at 106°. *Dibenzyl Oxalate*, $(C_6H_5 . CH_2O . CO)_2$, melts at 80°.

Sulphur Derivatives of Benzyl Alcohol are formed just like the sulphur compounds of the fat-alcohols (I, 147).

Benzyl Sulphydrate, Benzyl Mercaptan, $C_6H_5 . CH_2 . SH$. It is a liquid with a leek-like odor; boils at 194°, and at 20° has a specific gravity = 1.058 (A. **140**, 86).

Benzyl Sulphide, $(C_6H_5 . CH_2)_2S$, melting at 49°, when subjected to dry distillation yields *stilbene* (see this), *stilbene sulphide*, *dibenzyl* (see this), *thionessal* or *tetraphenylthiophene* (see this), and toluene. The *sulphone*, $(C_6H_5 . CH_2)_2SO_2$, melts at 150°. It results when the sulphoxide in glacial acetic acid is acted upon by $KMnO_4$ (B. **13**, 1284).

Benzyl Disulphide, $(C_6H_5CH_2)_2S_2$, melting at 71° (B. **20**, 15), results from the oxidation of benzyl sulphydrate in the air (A. **136**, 86).

Benzyl Dimethyl Sulphine Iodide, $C_6H_5CH_2S(CH_3)_2I$, is an orange-red colored compound (B. **7**, 1274).

Benzyl Sulphoxide, $(C_6H_5CH_2)_2SO$, melting at 133°, is formed by oxidizing benzyl sulphide with nitric acid (B. **13**, 1284).

Benzyl Sulphonic Acid, $C_6H_5 . CH_2 . SO_3H$, is a deliquescent crystalline mass; it is isomeric with toluene-sulphonic acid. The *potassium salt* is formed on boiling benzyl chloride with potassium sulphite. The *chloride* melts at 92° (B. **13**, 1287).

Benzyl Hyposulphurous Acid, $C_6H_5CH_2SSO_3H$, melts at 74° (B. **23**, R. 284).

Nitrogen Derivatives of the Phenyl-Paraffin Alcohols.

Phenyl Nitro-paraffins: When the homologous benzenes are heated in sealed tubes with dilute nitric acid the nitro groups usually enter the side chains with the formation of phenylnitroparaffins (see I, 154; Konowaloff, B. **28**, 1850, R. 235; **29**, 2199). By this treatment toluene yields *Phenylnitromethane*, $C_6H_5 . CH_2 . NO_2$. This body has also been prepared from nitrobenzalphthalide, as well as from benzyl haloids, but best from the iodide (B. **29**, 700) by the action of silver nitrite. It is an oil boiling with decomposition at 226°. It dissolves, like the nitro-paraffins, in sodium hydroxide, forming a sodium salt, from which the oily phenylnitromethane is again regained by the action of CO_2 or acetic acid. If, however, the sodium salt be precipitated with mineral acids, a crystalline substance, melting at 84°, is obtained. This is isomeric with the oily body and is distinguished from it by the red coloration it yields with ferric chloride, as well as by its electric conductivity. It quickly changes both in solution and when in a free state into the oily isomeride. Its constitution certainly corresponds to the formula adopted for the sodium salts of the nitro-paraffins (I, 155), from which, however, the corresponding free bodies in the fatty series have not been successfully isolated (Hantzsch and O. W. Schultze, B. **29**, 2251):

$$C_6H_5 . CH_2NO_2 \longrightarrow C_6H_5CH{-}NONa \longrightarrow C_6H_5 . CH{-}NOH$$

(in the second and third formulas the CH and N are joined by an O bridge; an arrow above leads from the last back to the first)

Neutral Oil — Melts at 84°; acid.

Similar stable and unstable isomerides have also been obtained from the nucleus homologues and substituted phenyl nitro-paraffins.

Phenyl-Paraffin Amines, Benzylamines.—(1) Alcoholic ammonia converts benzyl chloride into mono-, di-, and tri-benzylamines (B. **23**, 2971):

Benzylamine,	$C_6H_5CH_2NH_2$,	boils at 187°.
Dibenzylamine,	$(C_6H_5CH_2)_2NH$,	" " 300°.
Tribenzylamine,	$(C_6H_5CH_2)_3N$,	melts " 91°.

Most of the other methods of producing benzylamine are reactions,

which have been fully discussed in connection with the primary alkylamines.

Benzylamine is formed (2) by the reduction of phenylnitromethane, benzaldoxime, and benzylidene phenylhydrazone (B. **19**, 1928, 3232); (3) and (4) by heating benzaldehyde with ammonium formate or formamide (B. **19**, 2128; **20**, 104), together with di- and tribenzylamine; (5) by the reduction of benzonitrile (B. **20**, 1709) and (6) of benzothiamide (B. **21**, 51); (7) by saponifying benzylisocyanide or benzyl carbonimide, $C_6H_5CH_2NCO$ (B. **5**, 692), and (8) benzyl acetamide, $C_6H_5CH_2NHCOCH_3$ (B. **12**, 1297); (9) by the distillation of phenylamidoacetic acid, $C_6H_5CH(NH_2)CO_2H$ (B. **14**, 1969); and (10) by the action of caustic alkali and bromine upon α-toluamide. Benzylamine is a liquid, dissolving readily in water. It differs from its isomeric toluidine in being a strong base, which attracts CO_2 from the air.

Homologous Benzylamines are isomeric with corresponding alphylamines (p. 164). They are mostly formed by reducing nitriles with alcohol and sodium; some by the reduction of oximes or nitro-compounds, while others are obtained by the methods indicated under benzylamine.

		B. P.	
β-*Phenylethylamine*,	$C_6H_5 . CH_2 . CH_2NH_2$,	197°	(B. **26**, 1904).
α-Phenylethylamine,	$C_6H_5CH(NH_2)CH_3$,	187°	(B. **27**, 2306).
o-Tolubenzylamine,	$CH_3[2]C_6H_4[1]CH_2NH_2$,	201°	(B. **23**, 1026).
m-Xylylamine,	$CH_3[3]C_6H_4[1]CH_2NH_2$,	201°	(B. **23**, 3165).
[1′-Amino-1,4-dimethylphene],	$CH_3[4]C_6H_4[1]CH_2 . NH_2$,	195°	(B. **20**, 1710).
γ-Phenyl-propylamine,	$C_6H_5 . CH_2 . CH_2 . CH_2 . NH_2$,	221°	(B. **27**, 2309).
β-Phenyl-propylamine,	$CH_3 . CH(C_6H_5) . CH_2NH_2$,	210°	(B. **26**, 2875).
α-Phenyl-propylamine,	$CH_3 . CH_2 . CH(C_6H_5) . NH_2$,	205°.	
β-Phenyl-isopropylamine,	$C_6H_5CH_2 . CH(NH_2)CH_3$,	203°	(B. **20**, 618).
[1′-Amino-1,2,4-trimethylphene],	$(CH_3)_2[2,4]C_6H_3[1]CH_2 . NH_2$,	218°	(B. **21**, 3083).
ω-Mesitylamine,	$(CH_3)_2[3,5]C_6H_3[1]CH_2 . NH_2$,	218°	(B. **25**, 3013).
Cumylamine,	$(CH_3)_2CH[4]C_6H_4[1]CH_2NH_2$,	226°	(B. **20**, 2414).
		M. P.	
Cumobenzylamine,	$(CH_3)_3[2,4,5]C_6H_2[1]CH_2NH_2$,	64°	(B. **24**, 2409).
Hemimellibenzylamine,	$(CH_3)_3[3,4,5]C_6H_2[1]CH_2NH_2$,	123°	(B. **24**, 2411).

An optically active, lævorotatory base (B. **29**, 2313) has been isolated by means of its bitartrate from α-phenylethylamine, $C_6H_5\overset{*}{C}H(NH_2)CH_3$, containing an asymmetric C-atom.

Benzylalkyl- and benzylalphylamines, as well as benzylalkylammonium compounds, attach themselves to the true benzylamines.

Benzylaniline, $C_6H_5 . CH_2 . NH . C_6H_5$, melts at 32°, and is formed from aniline and benzyl chloride (A. **138**, 225), or by the reduction of benzylidene aniline with sodium in alcoholic solution (A. **241**, 330). When heated to 220° with sulphur it yields *thiobenzanilide*, and *benzenylamidothiophenol* at 250° (A. **259**, 300).

Dibenzylaniline, $(C_6H_5 . CH_2)_2 . N . C_6H_5$, melts at 67° (B. **20**, 1611).

Benzyl Chloramine (B. **26**, R. 188). *Dibenzyl Nitrosamine*, $(C_6H_5CH_2)_2N . NO$, melts at 61° (B. **19**, 3288). *Benzyl Methyl Nitramine*, $C_6H_5CH_2N(CH_3)NO_2$ (B. **29**, R. 95).

Benzyl Oxethylamine, $C_6H_5.CH_2.NH.CH_2.CH_2OH$, *picrate*, melting at 136°, results from the rupture of the phenyloxazoline ring, $C_6H_5 . C\begin{cases} O—CH_2 \\ N—CH_2 \end{cases}$ (see this), by sodium and alcohol (B. **29**, 2382).

The following representatives of the numerous benzylated acid amides and benzylated nitrogen derivatives of carbonic acid may be mentioned:

Benzylacetamide, $C_6H_5CH_2NHCOCH_3$, melts at 60° (B. **19**, 1286).

Dibenzyl Urea Chloride, $(C_6H_5CH_2)_2NCOCl$, is an oil (B. **25**, 1819).

Benzyl Urea, $C_6H_5CH_2NHCONH_2$, melts at 147°. Sym. and unsym. *dibenzyl urea* melt at 167° and 124° (B. **9**, 81). *Tri-* and *tetra-benzyl urea* melt at 119° and 85° (B. **25**, 1826).

Benzylthiourea melts at 164° (B. **24**, 2727; **25**, 817).

Dibenzyl Guanidine, $(C_6H_5CH_2NH)_2C:NH$, melts at 100° (B. **5**, 695).

Benzylisocyanate, Benzyl carbonimide, $C_6H_5CH_2N:CO$, is a liquid with penetrating odor. *Benzylcyanurate* melts at 157° (B. **5**, 692). *Benzyl Mustard Oil*, $C_6H_5CH_2$-$N:CS$, boils at 243° (B. **1**, 201). *Dibenzylhydrazine*, $C_6H_5.CH_2.NH.NH.CH_2.C_6H_5$, melting at 65°, is formed when benzalazine (p. 185) is reduced. It yields $(C_7H_7N_2)_2$ on oxidation. Concentrated acids resolve the latter into benzalazine and dibenzylhydrazine (B. **28**, 2345).

Benzylhydroxylamines.—Liquid *α-benzylhydroxylamine*, $C_6H_5CH_2O.NH_2$, boiling at 123° (50 mm.), results upon decomposing benzyl benzaldoxime with hydrochloric acid. Benzyl chloride changes this liquid substance to

αβ-Dibenzylhydroxylamine, $C_6H_5CH_2.O.NH.CH_2.C_6H_5$, liquid, and
Tribenzylhydroxylamine, $C_6H_5CH_2.O.N(CH_2.C_6H_5)_2$.

β-**Benzylhydroxylamine** is obtained by decomposing *αβ*-dibenzylhydroxylamine with hydrochloric acid. It melts at 57°. Benzyl chloride converts it into *β-dibenzylhydroxylamine*, $(C_6H_5CH_2)_2N.OH$, melting at 123° (A. **275**, 133); compare also the benzaldoximes, p. 185.

β-Bis-o-nitrobenzylhydroxylamine, $(NO_2.C_6H_4.CH_2)_2N.OH$, melting at 24°, is obtained from o-nitrobenzyl chloride and hydroxylamine. Nitrobenzylisonitrobenzaldoxime is formed by its oxidation (p. 187) (B. **30**, 58).

Substituted benzyl alcohols are derived from substituted benzyl chlorides when they are heated with aqueous potash (B. **25**, 3290), or by means of acetic esters. Many, like m-nitrobenzyl alcohol, are also obtained by the action of alcoholic potash upon the corresponding aldehydes.

o-, m-, p-Brombenzyl Alcohol:	o- melts at 80°; m- is liquid; p- melts at 72°.
o-, m-, p-Brombenzyl Bromide,	melt at 30°, 41°, 61°.
o-, m-, p-Nitrobenzyl Alcohol,	" " 74°, 27°, 93°.
o-, m-, p-Nitrobenzyl Chloride,	" " 47°, 46°, 71°.

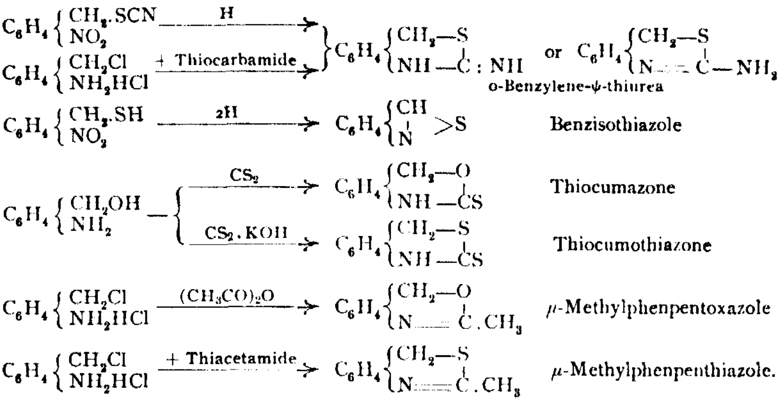
Formation of Hetero-rings from Derivatives of o-Amidobenzyl Alcohol.—Just like the o-diamines (p. 95), o-amidophenols (p. 152), and o-amidothiophenols (p. 157), many o-amidobenzyl alcohol derivatives, and also those of o-nitrobenzyl alcohol, so far as they yield o-amidobenzyl alcohol compounds upon reduction, show ability to form hetero-rings. Some of the derivatives of these two alcohols capable of yielding hetero-rings are the following:

o-*Nitrobenzyl Sulphocyanide*, $NO_2C_6H_4CH_2S.CN$, melting at 75° (B. **25**, 3028), yields o-benzylene-*ψ*-thiourea. Sulphuric acid reduces it to o-nitrobenzylcarbaminethiolic ester, $NO_2.C_6H_4CH_2.SCONH_2$, melting at 116°. Hydrochloric acid saponifies this to o-nitrobenzyl mercaptan, $NO_2[2]C_6H_4[1]CH_2SH$, melting at 43°. Both bodies yield *benzisothiazole* upon reduction (B. **28**, 1027; **29**, 160).

o-**Amidobenzyl Alcohol**, $C_6H_4(NH_2).CH_2.OH$, melting at 82° and boiling at 160°, is formed by the reduction of anthranil and o-nitrobenzyl alcohol with zinc-dust and hydrochloric acid (B. **25**, 2968; **27**, 3513). It becomes thiocumazone (B. **27**, 1866) when it is boiled with alcoholic CS_2, and thiocumothiazone (B. **27**, 2427) when the CS_2 and alcoholic potash are used. The urea derivatives of o-amidobenzyl alcohol lead to similar rings (B. **27**, 2413).

o-*Amidobenzyl Chloride Hydrochloride*, $HCl.NH_2.C_6H_4CH_2Cl$, is formed by the action of concentrated hydrochloric acid upon o-amidobenzyl alcohol. With caustic potash this salt yields poly-o-benzylene-imide, $(C_7H_7N)x$ (B. **19**, 1611; **28**, 918, 1651); with acetic anhydride, *μ*-methylphenpentoxazole, with thiacetamide *μ*-methylphenpenthiazole (B. **27**, 3515), and with thiurea, o-benzylene-*ψ*-thiurea (B. **28**, 1039); compare o-nitrobenzylrhodanide.

An anhydride of an o-*benzylalcohol sulphonic acid*, $C_6H_4\left\{\begin{array}{l}[1]SO_2\\ [2]CH_2\end{array}\right\rangle O$, melting with decomposition at 288°, has been obtained by reduction of o-sulphobenzoic chloride, just as phthalide has been formed from phthalyl chloride (B. **27**, R. 790).



o-**Nitrobenzylamine,** $C_6H_4(NO_2).CH_2.NH_2$, obtained from o-nitrobenzylchloride by the saponification of its phthalimide-derivative, is a strong, oily base (B. **20**, 2227).

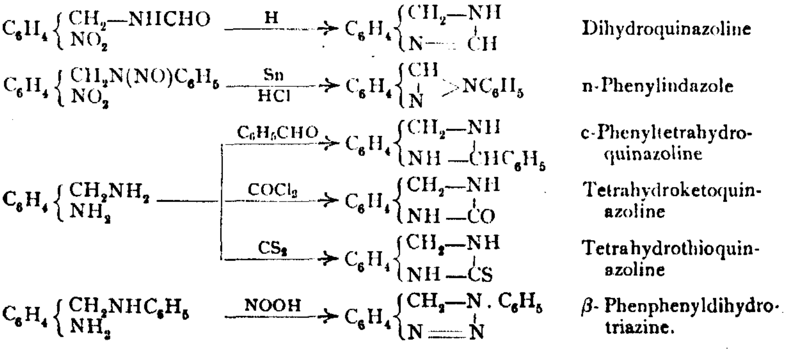
o-*Nitrobenzylformamide*, $NO_2.C_6H_4.CH_2.NH.CHO$, melting at 89°, is reduced to *dihydroquinazoline* (see this) (B. **25**, 3031).

p-*Nitrobenzylamine*—see B. **30**, 61.

o-*Nitrobenzyl Aniline*, $NO_2.C_6H_4.CH_2.NHC_6H_5$, melts at 44° (B. **19**, 1607).

o-*Nitrobenzylphenylnitrosamine*, $NO_2C_6H_4CH_2N(NO)C_6H_5$, is converted by tin and hydrochloric acid into n-*phenylindazole* (B. **27**, 2899).

o-*Amidobenzylamine*, o-benzylenediamine, $NH_2C_6H_4CH_2NH_2$, is a radiating crystalline mass, obtained from o-nitrobenzylamine. With aldehydes like benzaldehyde it forms *phenyltetrahydroketoquinazoline*; with phosgene, *tetrahydroketoquinazoline*; with carbon disulphide, *tetrahydrothioquinazoline* (B. **28**, R. 238). o-*Amidobenzyl Aniline*, $NH_2.C_6H_4.CH_2.NH.C_6H_5$, melting at 86°, forms *β-phenphenyldihydrotriazine* with nitrous acid (B. **25**, 448):



2. AROMATIC MONALDEHYDES.

The aromatic monaldehydes are the first oxidation products, and correspond to the primary aromatic monohydric alcohols. They are very similar to the fatty aldehydes so far as their rearrangements, dependent upon the reactivity of the aldehyde group, are concerned.

Formation.—(1) By the oxidation of the primary monohydric, aromatic alcohols. (2) By the distillation of the calcium salts of the aromatic acids with calcium formate. (3) From their halogen derivatives, $C_6H_5.CHCl_2$, with water, especially in the presence of sodium carbonate, lime, or lead oxide, or by heating with anhydrous oxalic acid. (4) Technically by oxidizing benzyl chloride with lead nitrate. (5) A very interesting and direct conversion of homologous benzenes into aldehydes is that occurring in the action of chromyl chloride, CrO_2Cl_2. The first products are pulverulent, brown addition-compounds, $C_6H_5CH_3(CrO_2Cl_2)_2$, which decompose into aldehydes when they are introduced into water (B. **17**, 1462; **21**, R. 714).

Properties.—Benzaldehyde and its homologues are mostly liquid bodies, which possess an aromatic odor and reduce ammoniacal silver solutions with the production of a metallic mirror. (1) They are readily oxidized to carboxylic acids. (2) They differ from the fatty aldehydes in that they are, as a general thing, readily oxidized to alcohols and acids by alcoholic or aqueous alkalies (p. 176); it appears that this reaction is, however, only peculiar to those aldehydes in which the CHO-group is in direct union with the benzene nucleus. (3) Nascent hydrogen reduces them to alcohols when they are in part, through the union of two aldehyde residues, converted into *hydrobenzoïns*. (4) They combine with acid alkaline sulphites. (5) With hydroxylamine they yield *aldoximes*, which manifest rather remarkable isomeric relations. (6) They form *phenylhydrazones* with phenylhydrazine. (7) Phosphorus pentachloride replaces their aldehyde oxygen by two atoms of chlorine. (8) Chlorine substitutes aldehyde hydrogen.

They do not polymerize, as do the first members of the group of fatty aldehydes.

Nucleus Syntheses.—(1) In the reduction of aromatic aldehydes—*e. g.*, in the electrolytic reduction (B. **29**, R. 229)—there occurs, along with alcohol formation, a production of hydrobenzoïn analogous to the pinacone formation (1, 212):

$$2C_6H_5.CHO + 2H = C_6H_5CH(OH) - CH(OH).C_6H_5\text{—Hydrobenzoïn.}$$

(2) A very interesting reaction of the aldehydes is their conversion into benzoïns through the agency of alcoholic potassium cyanide. Two aldehyde molecules combine to a polymeric body:

$$2C_6H_5CHO = C_6H_5CH(OH).CO.C_6H_5\text{—Benzoïn.}$$

See B. **29**, 1729, for the condensations of benzylidene aniline and benzaldehyde by potassium cyanide.

(3) The aromatic aldehydes combine with the most heterogeneous

bodies,—*e. g.*, aldehydes, ketones, monocarboxylic acids, dicarboxylic acids, etc.,—water always disappearing.

These so-called *condensation-reactions* proceed similarly to the *aldol*-condensation, only there is generally an elimination of water, as in the conversion of aldol into *croton-aldehyde*. The condensation agents are HCl-gas, zinc chloride, sulphuric acid, glacial acetic acid, acetic anhydride, dilute sodium hydroxide, baryta-water, a solution of potassium acetate, and potassium cyanide.

In this manner benzaldehyde can undergo the following rearrangements without difficulty:

$C_6H_5.CHO$ —	$\xrightarrow{CH_3COOH}$	$C_6H_5CH = CH.COOH$	Cinnamic Acid
	$\xrightarrow{CH_3CHO}$	$C_6H_5CH = CH.CHO$	Cinnamic Aldehyde
	$\xrightarrow{CH_3.CO.CH_3}$	$C_6H_5CH = CH.CO.CH_3$	Benzalacetone
	$\xrightarrow{CH_2(COOH)_2}$	$C_6H_5CH = C(COOH)_2$	Benzalmalonic Acid
	$\xrightarrow{CH_3COCH_2CO_2C_2H_5}$	$C_6H_5CH = C\begin{matrix} CO_2.C_6H_5 \\ CO.CH_3 \end{matrix}$	Benzalacetoacetic Ester.

Pyrones, $CO[C(CH_3):C(C_6H_5)]_2O$ (B. **29**, 1352), result when two molecules of benzaldehyde condense with ketones like diethylketone. *Pyridine* derivatives result when benzaldehyde and acetoacetic ester condense with ammonia and aniline; whereas benzylidene diacetoacetic esters are formed under the influence of aliphatic amines (B. **29**, R. 841).

The benzaldehydes also condense with phenols and anilines, forming derivatives of triphenylmethane.

The conditions under which these bodies are formed will be more fully explained in connection with their description.

Benzaldehyde, Bitter Almond Oil, *Benzyl Hydride*, $C_6H_5.CHO$, boiling at 179°, with sp. gravity 1.050 (15°), is a colorless liquid with high refractive power. Formerly it was prepared exclusively from its glucoside amygdalin (see below). At present it is only the officinal bitter-almond oil water, *aqua amygdalarum amararum*, in which hydrocyanic acid is the active ingredient, that is made from the amygdalin. It has the characteristic agreeable "bitter-almond oil" odor. It is soluble in 30 parts water, and is miscible with alcohol and ether. Benzaldehyde does not occur already formed in the bitter almonds, but is produced, as demonstrated by Wöhler and Liebig in 1831, from the glucoside *amygdalin*, contained in the oil. This is easily converted by boiling with dilute acids or upon standing in contact with the unorganized ferment *emulsin*, also present in bitter almonds, into benzaldehyde, glucose, and hydrocyanic acid. Amygdalin:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_6H_5CHO + 2C_6H_{12}O_6 + CNH.$$

In the general methods common to the formation of all aldehydes reactions were indicated which would lead to the production of benzaldehyde. Thus it is formed (1) from benzyl alcohol; (2) from calcium benzoate and formate; (3) from benzal chloride; (4) from benzyl chloride, from which it is prepared technically by oxidation with lead nitrate; and (5) from toluene and chromyl chloride, CrO_2Cl_2.

In describing the transformations of the aldehydes, benzaldehyde was

chosen as the example. It even absorbs oxygen from the air and becomes benzoic acid, and when mixed with acetic anhydride and sand it not only yields benzoic acid, but also *benzoyl peroxide* $(C_6H_5COO)_2$ (see this) (B. **27**, 1959). Sodium amalgam reduces it to benzyl alcohol and hydrobenzoïn, while PCl_5 changes it to benzal chloride. It shows both oxime and phenylhydrazone formation, etc.

Homologous Benzaldehydes.—o-, m-, and p-*Toluic Aldehydes* boil at 200°, 199°, and 204°. The o- and m-bodies smell like benzaldehyde, while the p-compound has an odor like that of pepper.

a-**Toluic Aldehyde, Phenylacetaldehyde,** $C_6H_5.CH_2.CHO$, boiling at 206° and isomeric with the three toluic aldehydes, is produced (1) by distillation of *a*-toluate of calcium and calcium formate; (2) when chromyl chloride and water act upon ethyl benzene; (3) by acting with water on *β*-bromstyrolene; (4) by heating phenyl-lactic acid or phenyl-glycidic acid with dilute sulphuric acid; (5) from phenyl-*a*-chlor-lactic acid, $C_6H_5.CH(OH).CHCl.CO_2H$, by the action of alkalies (B. **16**, 1286; A. **219**, 179); and (6) from phenyl-glyceric acid at 160°.

Phenyl-propyl Aldehyde, hydrocinnamic aldehyde, $C_6H_5.CH_2.CH_2.CHO$, boils at 208°.

Cumic Aldehyde, Cuminol, p-isopropyl-benzaldehyde, $(CH_3)_2CH-[4]C_6H_4[1]CHO$, boiling at 235°, with specific gravity 0.973 (13°), occurs, together with cymene, in Roman caraway oil, and in oil of *Cicuta virosa*, or water hemlock (B. **26**, R. 684). Cuminol possesses an aromatic odor. Dilute nitric acid oxidizes it to cumic acid; chromic acid converts it into terephthalic acid. *Cumic acid* (see this) and *cumyl alcohol* (p. 177) are produced when it is digested with alcoholic potash. When distilled with zinc-dust, cymene results.

Derivatives of Benzaldehyde.

Haloid Derivatives.—The halogen compounds corresponding to benzaldehyde are obtained by the action of PCl_5 or PBr_5 upon it.

Benzal Chloride, Benzylidene Chloride, Chlorobenzene, Chloride of Bitter-almond Oil, $C_6H_5CHCl_2$, boiling at 213°, with sp. gravity 1.295 (16°), results from the action of chlorine upon boiling toluene, from toluene (A. **139**, 318; **146**, 322) and PCl_5 at 170–200°, as well as from benzaldehyde and $COCl_2$ (Z. f. Ch. [2] **7**, 79). It changes to benzaldehyde when it is heated to 140–160° with water, or to 60–70° with anhydrous oxalic acid. *Benzal Bromide* boils at 130–140° (20 mm.).

Ethers and Esters of Benzaldehyde.—*Benzal dimethyl* and *diethyl ether*, boiling at 208° and 222°, *benzal diacetyl ester*, melting at 44° and boiling at 220° (A. **102**, 368; **146**, 323), are produced when sodium methylate, sodium ethylate, and silver acetate act upon benzal chloride. The diethyl ether is also formed from benzaldehyde and orthoformic ester (1, 233; B. **29**, 247), as well as from benzylideneimide hydrochloride with alcohol.

Sulphur Derivatives of Benzaldehyde.—Compare the thioacetaldehydes (1, 203): *a*- and *β*-*trithiobenzaldehyde* melt at 167° and 225° (B. **29**, 159). Polymeric *thiobenzaldehyde* melts at 83° (B. **24**, 1428). When heated with finely divided copper they yield *stilbene*, $C_6H_5.CH = CH.C_6H_5$ (see this). *Potassium Oxybenzylsulphonate*, $C_6H_5CH(OH)SO_3K + \frac{1}{2}H_2O$ (Bertagnini, A. **85**, 186).

Benzaldehyde Nitrogen Derivatives.—In its deportment toward ammonia benzaldehyde approaches formaldehyde more closely than it does acetaldehyde, in that it forms—

Hydrobenzamide, *tribenzal-diamine*, $(C_6H_5CH)_3N_2$, melting at 110°. When this body is heated it is transposed to *amarine* or *triphenyldihydroglyoxaline* (see this). When hydrochloric acid gas is conducted into the alcoholic benzene solution of hydrobenzamide, *benzylidene imide*, $C_6H_5CH:NH.HCl$, melting with decomposition at 180°, separates. Water immediately resolves this body into benzaldehyde and ammonium chloride (B. **29**, 2144).

Benzal Ethylamine, $C_6H_5 . CH : N . C_2H_5$, boils at 195°. **Benzal Aniline,** *Ben-ylidene Aniline*, $C_6H_5 . CH : N . C_6H_5$, melts at 45°.

When the o-phenylenediamines and benzaldehyde interact the bodies resulting at first re: *Benzylidene-o-phenylenediamine*, $NH_2 . C_6H_4N : CH . C_6H_5$, melting at 61°, and *ibenzylidene-o-phenylenediamine*, $C_6H_4[N : CH . C_6H_5]_2$. However, they readily rear-inge themselves into isomeric, ring-shaped imidazole derivatives or aldehydines (p. 96) B. **29**, 1497).

Benzylidene-hydrazine, $C_6H_5 . CH : NNH_2$, melting at 16° and boiling at 140° 14 mm.), and obtained from hydrazine hydrate with benzaldehyde and barium oxide J. pr. Ch. [2] **44**, 539), passes through a number of reactions, splitting off hydrazine, berating nitrogen, etc., until it finally becomes—

Benzalazine, $C_6H_5CH : N_2 : CH . C_6H_5$, melting at 93°. When this compound is eated it breaks down into nitrogen and *stilbene* (see this). It yields dibenzyl hydrazine p. 180) upon reduction, and combines with bromine to a *tetrabromide*, which decom-oses very readily, with evolution of nitrogen (B. **28**, 2345).

Benzal-phenylhydrazone, $C_6H_5CH : NNHC_6H_5$, melting at 152° (A. **190**, 134), ecomes dibenzaldiphenylhydrotetrazone when it is oxidized (p. 128).

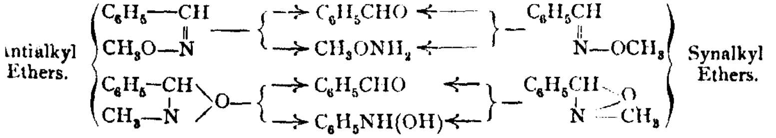
Numerous benzal-compounds of hydrazine derivatives have been prepared; they serve o characterize the latter.

Benzhydrazoïn, $C_6H_5 . CH \left< \begin{matrix} N . C_6H_5 \\ | \\ N . C_6H_5 \end{matrix} \right.$, melting at 55°, is formed from benzalde-yde and hydrazobenzene (p. 117), at 120°–150° (B. **19**, 2239).

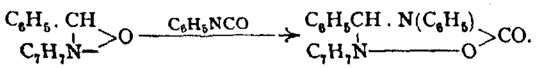
Benzaldoximes.—The interaction of hydroxylamine and benzaldehyde produces -*Benzaldoxime*, benzantialdoxime, melting at 35° and boiling at 117° (14 mm.). Iydrochloric acid, sulphuric acid, or bromine changes it, with the simultaneous produc-ion of unstable salts (B. **27**, R. 599), into *β Benzaldoxime*, isobenzaldoxime, benzsyn-ldoxime, melting at 125°. When this body is distilled under reduced pressure it passes nto the α-derivative. Each of these isomerides gives rise to two structurally isomeric eries of *alkyl ethers*, in one of which the alkyl is joined to oxygen, in the other to nitro-en, as the first, upon decomposition, yield α-, and the second β-alkyl hydroxylamines. Iantzsch and Werner attribute the isomerism of the α- and β-aldoximes to the spacial rrangement of the hydroxyl group with reference to nitrogen. The oximes are distin-uished as benzanti- and benzsynaldoxime (B. **24**, 3481). The syn-configuration would ıll to the β-aldoxime, because in a series of reactions—*e. g.*, treatment of the acid ester rith alkalies—it changes more readily and completely to *benzonitrile* than the α-body:

$$(\alpha\text{-})\ \text{Benzantialdoxime}\ \begin{matrix} C_6H_5 . CH \\ \| \\ HON \end{matrix} \qquad (\beta\text{-})\text{Benzsynaldoxime}\ \begin{matrix} C_6H_5CH \\ \| \\ NOH \end{matrix}$$

The following formulas would then correspond to the N- and O-alkyl ethers of these ompounds:



The benzaldoximes and phenylcyanate combine to isomeric phenylurethane deriva-ves, $C_6H_5CH : NOCONHC_6H_5$. The N-alkyl ethers also unite with phenylcyanate, ›rming azoxazole- (furo-ab′-diazole-) derivatives (B. **27**, 1957):



Antibenzaldoxime-o-methyl Ether is an oil, boiling at 191°. It results from the inter-ıction of α-benzaldoxime with sodium alcoholate and methyl iodide. Hydrochloric acid

resolves it into benzaldehyde and α-methylhydroxylamine. N-*Methyl Ether* melts at 45–49°. Its hydrobromide is formed on heating α-benzaldoxime, methyl bromide and methyl alcohol in a sealed tube to 85°. On exposure it rearranges itself into the syn-form (B. **29**, R. 866). *Synbenzaldoxime*-N-*methyl Ether*, melting at 82°, is formed, together with the isomeric o-ether (which appears not to have been isolated), from syn-benzaldoxime, methyl iodide, and sodium ethylate (B. **24**, 2812).

N-*Phenylbenzaldoxime*, $C_6H_5CH<\overset{O}{\underset{NC_6H_5}{|}}$, melting at 109°, results from the union of benzaldehyde with β-phenylhydroxylamine (p. 70) (B. **27**, 1958).

Benzantialdoxime Acetate, $C_6H_5CHNO(OC.CH_3)$, melts at 15° (B. **27**, R. 599).

Benzaldoxime-O-acetic Acid, $C_6H_5CHN(OCH_2COOH)$, melts at 98°, the N-*derivative*, $C_6H_5CH<\overset{N.CH_2.COOH}{\underset{O}{|}}$, at 183° with decomposition. They are formed when chloracetic acid acts upon potassium benzaldoxime. When decomposed the first yields glycollic acid and the second amidoxylacetic acid, $HO.NH.CH_2.COOH$ (I, 350) (B. **29**, R. 169).

Benzalamido-sulphonic acid, $C_6H_5.CH:NSO_3H$, results from benzaldehyde and amido-sulphonic acid (B. **25**, 472).

Many substituted benzaldoximes, ketoximes, the benzildioximes, etc., show isomeric relations similar to those exhibited by the benzaldoximes.

Substituted Benzaldehydes deport themselves toward oxidizing and condensing agents the same as benzaldehyde itself. The formation of heterocyclic bodies from o-nitro- and o-amidobenzaldehyde is especially worthy of notice.

Haloid Benzaldehydes are formed when oxalic acid or sulphuric acid (A. **272**, 148) acts upon the halogen benzal chlorides; or by oxidizing cinnamic acids containing halogens in the nucleus:

o-*Chlorbenzaldehyde*	melts at —4°;	boils at 213°;	the *oxime*	melts at	75°.
m-*Chlorbenzaldehyde*	" 17°;	" 213°;	"	"	70°.
p-*Chlorbenzaldehyde*	" 47°;	" 213°;	"	"	106°.
o-*Brombenzaldehyde*	" 21°;	o-*Iodbenzaldehyde*		"	37°.
p-*Brombenzaldehyde*	" 57°;	p-*Iodbenzaldehyde*		"	73°.

See B. **29**, 875, for the *di-* and *tetrachlorbenzaldehydes*.

o-, m-, p-*Iodosobenzaldehydes*, $C_6H_4(IO)CHO$, and o-, m-, and p-*Iodobenzaldehydes*, $C_6H_4(IO_2)(CHO)$, have been obtained from the corresponding iodide-chlorides (B. **29**, R. 774).

Nitrobenzaldehydes, $NO_2C_6H_4CHO$. On dissolving benzaldehyde in nitric-sulphuric acid, the chief product is meta-nitrobenzaldehyde. o-Nitrobenzaldehyde is formed simultaneously (B. **14**, 2803). o-Nitrobenzaldehyde is obtained pure from o-nitrocinnamic acid by oxidizing the alkaline solution with potassium permanganate in the presence of benzene (B. **17**, 121), or from o-nitrocinnamic ester through the action of nitric acid and sodium nitrite.

Para-nitrobenzaldehyde results (1) by the oxidation of p-nitrocinnamic acid (B. **14**, 2577); (2) by allowing CrO_2Cl_2 and water to act upon p-nitrotoluene in carbon disulphide (B. **19**, 1061); (3) when p-nitrobenzyl chloride is boiled with water and lead nitrate, or when sulphuric acid acts upon p-nitrobenzal chloride:

	M. P.		M. P.		M. P.
o-*Nitrobenzaldehyde*,	46°;	*oxime*,	97° (α), 136° (β);	*hydrazone*,	153°.
m-*Nitrobenzaldehyde*,	58°;	"	117° (α), 118° (β);	"	121°.
p-*Nitrobenzaldehyde*,	107°;	"	129° (α), 174° (β);	"	155°.

Compare B. **25**, 2457, for the deportment of the nitrobenzaldehydes in the animal organism. o-Nitrobenzaldehyde condenses with aldehyde and acetone through the action of dilute caustic soda to o-nitrophenyllactic acid aldehyde and o-nitrophenyllactic methyl ketone, which caustic soda converts into *indigo*:

$$C_6H_4\left\{\begin{matrix}{[1]}CHO\\ {[2]}NO_2\end{matrix}\right. - \left\{\begin{matrix} \xrightarrow{CH_3.CHO} C_6H_4\left\{\begin{matrix}CH(OH).CH_2.CHO\\ NO_2\end{matrix}\right. \\ \xrightarrow{(CH_3)_2CO} C_6H_4\left\{\begin{matrix}CH(OH).CH_2.CO.CH_3\\ NO_2\end{matrix}\right.\end{matrix}\right\} \rightarrow C_6H_4\left\{\begin{matrix}CO\\ NH\end{matrix}\right\rangle C:C\left\langle\begin{matrix}CO\\ NH\end{matrix}\right\} C_6H_4.$$

Indigo.

When the nitrobenzaldehydes are reduced electrolytically the first products are *aldehydophenylhydroxylamines*, $CHO.C_6H_4NHOH$, which, however, immediately combine with the unaltered nitrobenzaldehyde to N-*aldehydophenyl-nitrobenzaldoxime*, $NO_2C_6H_4CH\left\langle\begin{matrix}N.C_6H_4CHO\\ \mid \\ O\end{matrix}\right.$ (p. 185) (B. **29**, 3037; **28**, 250). Ferric chloride oxidizes this condensation-product to *nitrosobenzaldehyde*, $NO.C_6H_4.CHO$.

N-o-*Nitrobenzyl*-o-*nitrobenzaldoxime*, $NO_2.C_6H_4.CH\left\langle\begin{matrix}N.CH_2.C_6H_4.NO_2\\ \mid \\ O\end{matrix}\right.$, melting at 142°, results upon oxidizing bis-o-nitrobenzylhydroxylamine (p. 180) (B. **30**, 58).

5-*Nitro*-2-*chlorbenzaldehyde*, $NO_2.C_6H_3Cl.CHO$, melts at 80°; its *oxime* at 147°. The latter is readily converted by boiling alkali into nitrosalicylic acid (B. **26**, 1253). 3-*Nitro*-4-*brombenzaldehyde*, $NO_2.C_6H_3BrCHO$, melts at 103°; its *oxime* at 145° (B. **24**, 3775).

Amidobenzaldehydes, $NH_2C_6H_4CHO$. The o- and p- bodies are obtained in the action of ferric chloride upon their oximes, which are formed by the reduction of o- and p-nitrobenzaldoximes with ammonium sulphide (B. **15**, 2004; **16**, 1998).

o-**Amidobenzaldehyde** is also obtained by reducing o-nitrobenzaldehyde and *anthranil* (see this) with ferrous sulphate and ammonia (B. **17**, 456). m-Amidobenzaldehyde is formed when m-nitrobenzaldehyde is reduced with tin and glacial acetic acid.

o-Amidobenzaldehyde	melts at 39°;	its *oxime* at 132°;	its *acet-derivative* at 70°.
m-Amidobenzaldehyde is yellow and amorphous;		" 88°;	" " —.
p-Amidobenzaldehyde	melts at 70°;	" 124°;	" " 155°.

p-*Dimethyl*- and p-*Diethylamidobenzaldehydes*, melting at 73° and 81°, are obtained when the condensation-products from chloral and dialkyl aniline—*e.g.*, p-dimethylamidophenyl-trichlorethyl alcohol, $(CH_3)_2NC_6H_4CH(OH)CCl_3$—are acted upon with alcoholic potash (B. **19**, 365). p-Dimethylamidobenzaldehyde condenses to *hexamethylleucaniline* (see triphenylmethane dyes) with dimethylaniline.

The Hetero-ring Formations of o-*Amidobenzaldehyde*.—o-Amidobenzaldehyde combines especially readily with compounds containing a CH_2–CO group, in the presence of dilute caustic soda. The products resulting at first are of an aldol nature, for they immediately split off water and yield quinoline or its derivatives. o-Amidobenzaldehyde combines with acetaldehyde to *quinoline*, with acetone to *quinaldine*, with malonic acid to *β-carbostyril carboxylic acid* (B. **25**, 1752), and with urea to *quinazolon* (B. **28**, 1037). Alcoholic ammonia transposes the acidyl-o-amidobenzaldehydes into quinazolines or benzmetadiazines (B. **27**, 280, 443):

$$C_6H_4\left\{\begin{matrix}{[1]}CHO\\ {[2]}NH_2\end{matrix}\right. - \left|\begin{matrix} \xrightarrow{CH_3.CHO} C_6H_4\left\{\begin{matrix}CH = CH\\ N = CH\end{matrix}\right. \\ \xrightarrow{(CH_3)_2CO} C_6H_4\left\{\begin{matrix}CH = CH\\ N = C - CH_3\end{matrix}\right. \\ \xrightarrow{CH_2(CO_2H)_2} C_6H_4\left\{\begin{matrix}CH = C - COOH\\ N = C(OH)\end{matrix}\right. \\ \xrightarrow[-NH_3,\,-H_2O]{CO(NH_2)_2} C_6H_4\left\{\begin{matrix}CH = N\\ NH - CO\end{matrix}\right.\end{matrix}\right.$$

Quinoline

Quinaldine

β-Carbostyril Carboxylic Acid

Quinazolon

$$C_6H_4\left\{\begin{matrix}{[1]}CHO\\ {[2]}NH.CO.CH_3\end{matrix}\right. \xrightarrow{NH_3} C_6H_4\left\{\begin{matrix}CH = N\\ N = C.CH_3\end{matrix}\right.$$

Phen-β-methylmetadiazine, α-Methylquinazoline.

Benzaldehyde-m-*Sulphonic Acid*, $SO_3H . C_6H_4 . CHO$, white, deliquescent crystals (B. **24**, 791).

3. AROMATIC MONO-KETONES.

The oxidation products of the secondary phenyl-paraffin alcohols are ***mixed ketones***, in which an aromatic and an aliphatic hydrocarbon residue are joined by the CO-group. The ketones containing two benzene residues linked by carbonyl, such as benzophenone or diphenylketone, will be discussed later in connection with the corresponding hydrocarbons, like diphenylmethane.

Formation.—Mixed aromatic-aliphatic ketones are usually produced by reactions similar to those employed with the aliphatic ketones (1, 209):

(1) By the oxidation of secondary alcohols, like phenylmethyl carbinol.

(2) When sulphuric acid acts upon phenyl acetylene:

$$C_6H_5C : CH \longrightarrow C_6H_5COCH_3.$$

Nucleus-synthesis: (3) By the distillation of a mixture of calcium salts of an aromatic and a fatty acid. (4) By the action of zinc alkyls on acid chlorides (A. **118**, 20). (5) From benzenes by action of fatty acid chlorides and aluminium chloride, carbon disulphide being used as a diluent.

(6) By decomposing β-ketone carboxylic acids—*e. g.*, mono- and dialkyl benzoylacetic acids (B. **16**, 2131)—with alcoholic potash.

(7) Acidylated benzenes finally result as a consequence of intramolecular rearrangement upon heating the alkyl ethers of phenylolefine alcohols, which are prepared by the distillation of ortho-ethers of acetophenone. In this way the acidyl benzenes can be built up from acetophenone (Claisen, B. **29**, 2931):

$$C_6H_5CO . CH_3 \rightarrow C_6H_5C(OCH_3)_2 . CH_3 \rightarrow C_6H_5C(OCH_3) : CH_2 \rightarrow C_6H_5COCH_2 . CH_3.$$

Properties and Deportment.—The mixed aromatic-aliphatic ketones are colorless liquids, insoluble in water, and possess an odor which is not disagreeable.

(1) Nascent hydrogen converts them into secondary alcohols.

(2) Chromic acid transforms the ketones $C_6H_5 . COR$ into benzoic acid and the alkyl, which is further oxidized.

(3) Potassium permanganate converts them into α-ketonic acids (B. **23**, R. 640; **24**, 3543; **26**, R. 191).

(4) Acids and acid amides, strangely enough, are formed when phenylmethyl ketones are heated with yellow ammonium sulphide:

$$C_6H_5 . CO . CH_3 \text{ yields } C_6H_5 . CH_2 . CO_2H \text{ and } C_6H_5 . CH_2 . CO . NH_2.$$

(5) On heating benzene ketones with sulphuric acid the acetyl-group splits off and benzene sulphonic acids result (B. **19**, 2623).

(6) Those ketones in which the CO-group is attached to the benzene nucleus *do not* unite with alkaline bisulphites.

(7) The phenyl-alkyl ketones apparently form but *one* acetoxime with hydroxylamine; the opposite is true of benzaldehyde.

(8) They form *hydrazones* with phenylhydrazine.

Acetophenone, *Phenylmethyl Ketone, Acetyl Benzene,* $C_6H_5 . CO . CH_3$, melting at 20° and boiling at 202°, crystallizes in large plates. It is applied as a hypnotic under the name of *hypnone.* It is formed (1) from phenylmethyl carbinol; (2) from phenylacetylene; (3) by distilling benzoate of calcium with calcium acetate; (4) by the action of zinc methyl upon benzoyl chloride; (5) from benzene, acetyl chloride, and $AlCl_3$; (6) from benzoyl acetoacetic ester, $C_6H_5CO . CH(COCH_3) . COOC_2H_5$, and benzoyl acetic ester. The methods 3 and 5 are employed in its preparation.

Nascent hydrogen converts it into phenylmethyl carbinol. Chromic acid oxidizes it to benzoic acid, and potassium permanganate to phenylglyoxylic acid.

Acetophenone, like acetone, has been introduced into numerous nucleus-synthetic reactions. Some of the simplest of these will be given. It may be condensed to *dypnone* (see this) and to [1,3,5]-*triphenylbenzene*, two bodies bearing the same relation to acetophenone that mesityl oxide and mesitylene sustain to acetone.

Acetophenone also condenses in the most varied proportions with benzaldehyde, forming benzalacetophenone, benzaldiacetophenone, and dibenzal-triacetophenone (B. **29**, 1488). It yields the nitrile of α-phenyllactic acid with hydrocyanic acid. At higher temperatures chlorine enters the methyl group; PCl_5 substitutes the ketone-oxygen-producing *acetophenone chloride* (A. **217**, 105). Amyl nitrite and sodium ethylate convert acetophenone into *isonitrosoacetophenone*, which will be described under *Phenylglyoxal.*

Ortho-ethers of Acetophenone, like Acetophenone Ortho-ethyl Ether, $C_6H_5C(OC_2H_5)_2CH_3$, boiling at 107° (17 mm.), are prepared from acetophenone and orthoformic ethers (1, 233) (B. **29**, 2932). When heated under ordinary pressure they lose alcohol and pass into alkyl ethers of phenylolefine alcohols. They yield anils with aniline: *Acetophenone-anil*, $C_6H_5C:(NC_6H_5)CH_3$, melts at 41° and boils at 310°.

Acetophenone Oxime, $C_6H_5 . C:(N . OH) . CH_3$, melts at 59°. It is only known in one modification (B. **24**, 3482). By the action of concentrated sulphuric acid, or of HCl in glacial acetic acid, it is converted into acetanilide, $C_6H_5 . NH . CO . CH_3$ (p. 82). This remarkable intramolecular atomic rearrangement was discovered by Beckmann (Beckmann's Transposition, B. **20**, 2580; **23**, 2746).

Other ketoximes behave in an analogous manner. The reaction has been applied in determining the point of double union in the higher olefine monocarboxylic acids (1, 284), and for the decomposition or rupture of ring ketones.

Acetophenone Phenylhydrazone melts at 105°.

Acetophenone Homologues.—These are numerous and can be arranged in two groups: A. Ketones whose CO-group is attached to the benzene ring: *acidylated benzenes.* B. Ketones whose CO-group is not in immediate union with the benzene ring: *phenylated fatty ketones.*

A. *Acidylated benzenes* have been made especially by the general methods 3, 5, 6, and 7 (p. 188). At first some of the ketones were considered as *benzoyl-paraffins* and *cycloparaffins*, and others as *homobenzoylated paraffins:*

Propiophenone, Propionyl Benzene, boils at 210°; its *oxime* melts at 53° and boils at 165° (38 mm.) (B. **26**, 1427).

Butyrophenone, Benzoyl Propane, ... boils at 222°.
Butyl Phenyl Ketone, Benzoyl Butane, ... " 237°.
Isobutylphenyl Ketone, ... " 230°.
Isoamylphenyl Ketone, ... " 240°.
Diethyl Acetophenone, $C_6H_5CO . CH(C_2H_5)_2$, . . . " 230°.
Hexyl Phenyl Ketone, ... melts at 17° and " 155° (15 mm.).

Laurobenzene, $C_6H_5CO \cdot C_{11}H_{23}$, melts at 47° (B. **28**, R. 648).

Palmityl Benzene, $C_6H_5 \cdot CO \cdot C_{15}H_{31}$, melts at 59° and boils at 251° (15 mm.).

Benzoyl Trimethylene, $C_6H_5CO \cdot CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, formed on heating trimethylene benzoyl acetic acid to 200°, boils at 239°. Its *oxime* melts at 88°.

Benzoyl Tetramethylene, $C_6H_5COCH<\begin{matrix}CH_2\\CH_2\end{matrix}>CH_2$, from the chloride of tetramethylene carboxylic acid, boils at 258° (B. **25**, R. 372).

Nucleus-acidylated Alkyl Benzenes, homobenzoylated Paraffins.—p-Acetyl toluene is produced when concentrated nitric acid acts upon cymene (p. 56), and acetyl-3,4-(o)-xylene is formed from camphor by the action of concentrated sulphuric acid (B. **26**, R. 415):

p-*Acetyl Toluene*, $CH_3CO[4] \cdot C_6H_4[1] \cdot CH_3$,	boils at	224°.
1-*Acetyl*-3,4-(o)-*xylene*, ...	"	246°.
1-*Acetyl*-2,4-(m)-*xylene*, ...	"	247°.
Acetyl-p-*xylene*, ...	"	224°.
Acetyl-mesitylene, ...	"	235° (B. **24**, 3542).
1-*Acetyl*-2,4,5,6-*durene*, . . . melts at 73° and	"	260° (B. **29**, 847).

B. **Phenylated Fatty Ketones** have been prepared by methods 3, 4, and 6 (p. 188):

Phenyl Acetone, Benzyl Methyl Ketone, $C_6H_5 \cdot CH_2 \cdot CO \cdot CH_3$,	boils at	215°.
Benzyl Ethyl Ketone, $C_6H_5 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_3$, ...	"	226°.
Benzyl Acetone, $C_6H_5CH_2 \cdot CH_2 \cdot CO \cdot CH_3$, ...	"	235° (B. **14**, 889).

Substituted Acetophenones: *Haloid acetophenones*. Acetophenones containing halogens in the methyl group will be discussed after the corresponding oxygen derivatives: *benzoyl carbinol* (see this), *phenyl glyoxal* (see this), and *phenylglyoxylic acid* (see this). p-Haloid acetophenones, like $Cl \cdot C_6H_4 \cdot CO \cdot CH_3$, have been obtained from haloid benzenes, acetyl chloride, and aluminium chloride (compare haloid thiophene ketones) (B. **24**, 997, 3766):

p-*Chloracetophenone*, Acetyl-p-chlorbenzene, melts at 20° and boils at 230° (B. **18**, R. 502).
p-*Bromacetophenone*, Acetyl-p-brombenzene, melts at 51°.
p-*Iodacetophenone*, Acetyl-p-iodbenzene, melts at 83°.

Nitro-acetophenones.—The meta-body is the chief product (just as in the case of benzaldehyde) when acetophenone is dissolved in fuming nitric acid; at 30–40° o-nitroacetophenone predominates (B. **18**, 2238). The three isomerides can be prepared from the three nitrobenzoyl-acetoacetic esters (see these) (A. **221**, 323).

p-Nitroacetophenone is formed when concentrated sulphuric acid acts upon p-nitrophenylpropiolic acid (see this), through the rearrangement of the nitrophenylacetylene, formed at first, by water (A. **212**, 160) (see method of formation 2, p. 188).

o-**Nitro-acetophenone** is an oil of peculiar odor.

m-**Nitro-acetophenone** melts at 93°, and its *oxime* at 131° (B. **15**, 3063).

p-**Nitro-acetophenone** melts at 80°.

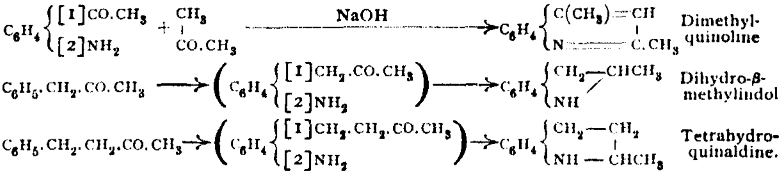
Amido-acetophenones, $C_6H_4(NH_2) \cdot CO \cdot CH_3$.

o-, m-, and p-**Amido-acetophenone** are obtained: By reducing o-nitroacetophenone (A. **221**, 326); from o-amido-phenyl acetylene, $C_6H_4(NH_2)C \vdots CH$, by the action of sulphuric acid (B. **17**, 964); by boiling o-amidophenyl-propiolic acid with water (B. **15**, 2153); and a slight quantity on heating aniline with acetic anhydride (B. **18**, 2688). o-*Amidoacetophenone* is a thick, yellow oil, which boils at 242–252°, and possesses a characteristic sweetish odor. m-**Amido-acetophenone** melts at 93°. p-**Amido-acetophenone** melts at 106°; its *oxime* melts at 147° (B. **20**, 512). A pine splinter dipped into the aqueous solution of o-amidoacetophenonehydrochloride is colored an intense orange-red.

Hetero-ring Formations of the Aromatic o-Amido-Ketones.

Dimethyl quinoline is produced (B. **19**, 1037) when o-amidoacetophenone is digested with acetone and sodium hydroxide. Oily nitro-compounds are formed in the nitration

of phenylacetone (p. 190) and benzylacetone. They yield, by reduction, β-methyldihydro-ketol and tetrahydroquinaldine (B. **14**, 889), as the o-amido-bodies (probably the o-amido-alcohols) produced at first sustain an intramolecular anhydride formation :



Acetophenone Sulphonic Acid, $SO_3H.C_6H_4.CO.CH_3$ (B. **19**, 2626).

4. AROMATIC MONOCARBOXYLIC ACIDS.

The aromatic carboxylic acids result upon replacing the hydrogen in benzene or its homologues by the carboxyl group. This group in these new derivatives is directly linked, as in the benzene carboxylic acids, to the benzene ring or it replaces the hydrogen of a side-chain :

$C_6H_5.CO_2H$ Benzoic Acid	$C_6H_4(CO_2H)_2$ Phthalic Acids	$C_6H_3(CO_2H)_3$ . . . Benzene Tricarboxylic Acids	. $C_6(CO_2H)_6$ Mellitic Acid.
$CH_3.C_6H_4CO_2H$ Toluic Acids	$(CH_3)_2C_6H_3CO_2H$ Xylic Acids.	$C_6H_5CH_2CO_2H$ Phenylacetic Acid α-Toluic Acid	$C_6H_5CH_2CH_2CO_2H$ Hydrocinnamic Acid β-Phenylpropionic Acid.

Only the mono-carboxylic acids will be now discussed, after the monohydric aromatic alcohols.

General Methods of Formation.—(1) While the aliphatic monocarboxylic acids or the paraffin carboxylic acids could not be obtained by the oxidation of the paraffins, the aromatic acids can be readily obtained from the benzene homologues by oxidizing the side-chains to carboxyl groups. The importance of this reaction in establishing constitution has been previously alluded to (p. 52). The most suitable oxidants are chromic acid, dilute nitric acid, potassium permanganate, and potassium ferricyanide.

(*a*) *Oxidation with Chromic Acid.*—Only the *para-* and *meta-derivatives* (the former more readily than the latter) of benzenes, carrying two side-chains, are oxidized to acids by chromic acid, while the ortho- are either not attacked at all or are completely destroyed.

In substituted alkyl benzenes the alkyl-group is prevented from being oxidized by chromic acid, if a negative group occupying the o-position with reference to the alkyl-group is present (B. **15**, 1021). The oxidations are conducted either with free chromic acid in glacial acetic acid, or with a mixture of potassium bichromate (3 parts) and sulphuric acid (3 parts), diluted with 2–3 volumes of water.

(*b*) *Oxidation with Nitric Acid.*—When oxidizing with nitric acid use acid diluted with 3 parts of water and boil for some time, in connection with a return condenser (2–3 days). Konowaloff (p. 178) contends that phenylnitroparaffins are first produced ; these then are further oxidized to carboxylic acids. To remove the nitro-acids which are invariably formed, the crude product is digested with tin and concentrated hydrochloric acid ; this converts the nitro- into amido-acids, which dissolve in hydrochloric acid.

In the derivatives with two different alkyls the higher alkyl is usually attacked first, by nitric acid or chromic acid ; sometimes ketones are present in the intermediate products (see Cymene, p. 56).

(*c*) Potassium permanganate often effects the oxidation at ordinary temperatures.

Ortho diderivatives may also be subjected to oxidation, without having the complete destruction of the benzene nucleus follow as a consequence.

(*d*) Potassium ferricyanide oxidizes methyl to carboxyl, if the nitro-group occupies the ortho-position relatively to the methyl-group. This does not occur if the nitro-group holds the meta-position (B. 22, R. 501).

(2) Oxidation of the corresponding aromatic alcohols and aldehydes.

(3) By the addition of hydrogen to the unsaturated monocarboxylic acids. Cinnamic acid becomes hydrocinnamic acid.

(4) By the reduction of phenylated oxyfatty acids, haloid aromatic acids, and ketone carboxylic acids.

1. $C_6H_5.CH_3 \xrightarrow{3O} C_6H_5.COOH$
2. $C_6H_5.CH_2OH \longrightarrow C_6H_5CHO \longrightarrow C_6H_5.COOH$
3. $C_6H_5.CH=CH.COOH \xrightarrow{2H} C_6H_5.CH_2.CH_2.COOH$
4. $C_6H_5.CH(OH).COOH \xrightarrow{2HI} C_6H_5.CH_2.COOH$
   $C_6H_5.CO.CO_2H \xrightarrow{4HI} C_6H_5.CH_2.COOH$
   $C_6H_5.CHCl.COOH \xrightarrow{2H} C_6H_5.CH_2.COOH.$

Nucleus-synthetic Reactions:

(5) Action of sodium and CO_2 upon monobrombenzenes (Kekulé).

(6) A similar reaction is that of sodium and esters of chlorcarbonic acid upon phenols and bromhydrocarbons (Würtz).

(7) Fusion of salts of the sulphonic acids with sodium formate.

(8) The action of phosgene gas upon benzenes in the presence of aluminium chloride; at first acid chlorides are produced.

(9) Urea chlorides, in the presence of $AlCl_3$, act in an analogous manner upon the benzenes. Acid amides are the first products. The urea chlorides can be replaced by cyanuric acid, by nascent cyanic acid, and by carbanile.

(10) By the synthesis of the acid nitriles—

(*a*) upon fusing the sulphonates with potassium cyanide;

(*b*) by action of potassium cyanide upon the phenylalkyl chlorides;

(*c*) when the bromnitrobenzenes are heated with potassium cyanide;

(*d*) when diazo salts are treated with potassium cyanide and copper sulphate;

(*e*) by heating the isonitriles alone.

The nitriles are changed to carboxylic acids when they are heated with mineral acids or alkalies.

Nucleus Syntheses:

5. $C_6H_5Br + CO_2 + 2Na \longrightarrow C_6H_5COONa + NaBr$
6. $C_6H_5Br + ClCO_2C_2H_5 + 2Na \longrightarrow C_6H_5COOC_2H_5 + NaCl + NaBr$
7. $C_6H_5SO_3Na + HCOONa \longrightarrow C_6H_5COONa + HSO_3Na$
8. $C_6H_6 + COCl_2 \xrightarrow{Al_2Cl_6} C_6H_5.COCl + HCl$

9*a*. $C_6H_6 + Cl.CONH_2 \xrightarrow{Al_2Cl_6} C_6H_5CONH_2 + HCl$
b. $C_6H_6 + CONH \longrightarrow C_6H_5CONH_2$
c. $C_6H_6 + CO.NC_6H_5 \longrightarrow C_6H_5CONHC_6H_5$

10*a*. $C_6H_5SO_3K + CNK \longrightarrow C_6H_5CN + SO_3K_2$
b. $C_6H_5CH_2Cl + CNK \longrightarrow C_6H_5.CH_2CN + KCl$
c. $C_6H_4BrNO_2 + CNK \longrightarrow C_6H_4(NO_2)CN + KBr$
d. $C_6H_5N_2Cl + CNK \longrightarrow C_6H_5CN + N_2 + KCl$
e. $C_6H_5.NC \longrightarrow C_6H_5CN.$

(11) Action of benzyl chloride upon sodium acetoacetic ester, and the decomposition of the ketonic esters—*e. g.*, benzyl acetoacetic ester—by alkalies.

(12) The decomposition of phenyl substitution products of the malonic acid series—*e. g.*, benzylmalonic acid—by heat.

(13) Action of metallic sodium upon the acetates, propionates, etc., of the phenyl carbinols: benzyl acetate yields phenylpropionic benzyl ester and phenylacrylic acid, while benzyl phenyl-butyric ester and phenylcrotonic acid are obtained from benzylpropionate (A. 193, 321; 204, 200):

$$4\begin{array}{l}COOCH_2 . C_6H_5\\ | \\ CH_3\end{array} + 2Na = 2\begin{array}{l}COOCH_2 . C_6H_5\\ | \\ CH_2 . CH_2 . C_6H_5\end{array} + 2\begin{array}{l}CO_2Na\\ | \\ CH_3\end{array} + H_2$$

$$2\begin{array}{l}CO . OCH_2 . C_6H_5\\ | \\ CH_2 . CH_2 . C_6H_5\end{array} + 2Na = 2\begin{array}{l}COONa\\ | \\ CH = CH . C_6H_5\end{array} + 2C_6H_5CH_3 + H_2.$$

Occurrence, Properties, and Deportment.—The aromatic acids occur naturally, partly in a free state, partly in many resins and balsams, and in the animal organism (see benzoic acid). They arise also in the decay of albuminoid bodies (see hydrocinnamic acid) (B. 16, 2313).

The aromatic acids are crystalline solids, which generally sublime undecomposed. Most of them dissolve with difficulty in water, hence are precipitated from their salt solutions by mineral acids. Sodium amalgam or zinc-dust will reduce some to aldehydes, and heating with concentrated hydriodic acid or phosphonium iodide converts them into hydrocarbons. When heated with lime or soda-lime, their carboxyl-groups are eliminated and hydrocarbons result (compare methane, 1, 80).

From the polycarboxylic acids we obtain, as intermediate products, acids having fewer carboxyl groups—*e. g.*, phthalic acid first yields benzoic acid and then benzene.

The hydrogen of the benzene nucleus in the acids can sustain substitutions similar to those observed with the hydrocarbons and phenols by the halogens, and the groups NO_2, SO_3H, NH_2, OH, etc. In other respects they are very similar to the fatty acids, and afford corresponding derivatives by the alterations of the carboxyl group.

Benzoic Acid, *Phenyl Formic Acid,* $C_6H_5 . COOH$, melting at 120° and boiling at 250°, occurs free in some resins, especially in gum benzoïn (from *Styrax benzoïn*), in dragon's blood (from *Dæmonorops Draco*), also in Peru and tolu balsams, where it exists in the form of its benzyl ester. It is found as hippuric acid in the urine of herbivoræ.

It is produced by the general methods 1 and 2 (pp. 191, 192) from toluene, benzyl alcohol, and benzaldehyde upon oxidation, as well as from all hydrocarbons, alcohols, aldehydes, ketones, and carboxylic acids and their derivatives, which are obtainable from benzene by the replacement of *one* hydrogen atom by a univalent side-chain. Benzoic acid can also be prepared by the oxidation of pure benzene; this is very probably due to the oxidation of diphenyl, which is formed at first (A. 221, 234). Toluene can also be changed to benzyl chloride, and this then be oxidized (see preparation) to benzoic acid, or benzotrichloride may be heated with water, concentrated sulphuric acid, or anhydrous oxalic acid, and the product will be benzoic acid. It can also be obtained, by the nucleus-synthetic reactions 5 and 10, from benzene,

brombenzene, sodium benzene sulphonate, and from aniline through diazobenzene chloride or phenylcarbylamine (p. 193). Finally, CO_2 can be added to benzene by means of aluminium chloride, and benzoic acid will result.

History.—Benzoic acid was obtained from gum benzoïn by sublimation, in the beginning of the 17th century. In 1775 Scheele showed how the acid could be extracted from the gum with lime-water, and then be precipitated from the solution of its calcium salt. In 1832 Liebig and Wöhler, in the course of their classic research upon the radical benzoyl, determined the elementary composition of the acid and illustrated its connection with benzaldehyde, as well as pointed out the simplest transformation products of the acid. This investigation produced such a profound impression upon the great master, Berzelius, that he proposed as a substitute for the name benzoyl—the name of the new radical containing more than two elements—that of *proïn* or *orthrin*, from the Greek words, πρωί, the beginning of day, or ὄρθρος, morning dawn, because a new day was now breaking for organic chemistry. In 1834 Mitscherlich distilled benzoic acid with lime and got benzene, which led him to regard the acid as a derivative of this hydrocarbon. From that day, and especially since the establishment of the benzene theory by Aug. Kekulé, benzoic acid has been serving in constantly increasing amount as the starting-out material for the preparation of innumerable products. It is the acid which has been most exhaustively investigated. The study of its derivatives has been greatly facilitated by the fact that the great crystallizing power of the acid has been transferred to most of its compounds (1, 271).

Preparation.—Gum benzoïn is sublimed or the resin is boiled with milk of lime, and the benzoic acid precipitated with hydrochloric acid. A more advantageous method is the production of the acid from hippuric acid. To accomplish this, boil the latter with concentrated hydrochloric acid. It is also produced when benzyl chloride is boiled with dilute nitric acid (B. 10, 1275). Benzoic acid results from phthalic acid by heating its calcium salt to 350° with calcium hydroxide.

Properties and Deportment.—Benzoic acid crystallizes from hot water, in which it is very soluble, in white, shining leaflets. It sublimes readily, and is carried over with steam. It dissolves with difficulty in cold water (1 part in 600 parts at 0°). Its vapors possess a peculiar odor, which produces coughing and sneezing. The officinal benzoic acid is obtained by the sublimation of Siam gum benzoïn.

The acid yields benzene and carbon dioxide when heated with lime. Benzoic acid, upon reduction, can yield *tetra-* and *hexa-hydrobenzoic acids* (see these).

Salts.—The *benzoates* are mostly quite readily soluble in water. Ferric chloride throws out a reddish precipitate of ferric benzoate from their neutral solutions.

The *potassium salt*, $2C_7H_5KO_2 + H_2O$, crystallizes in concentrically grouped needles. The *calcium salt*, $(C_7H_5O_2)_2Ca + 3H_2O$, consists of shining prisms or needles. The *silver salt*, $C_7H_5AgO_2$, crystallizes from hot water in bright leaflets.

Homologues of Benzoic Acid.—These compounds, like the homologues of benzaldehyde and acetophenone, can be arranged into two groups: *alkyl benzoic acids*, in which the CO_2H-group is attached to the benzene nucleus, as in benzoic acid itself, and *phenyl fatty acids*, in which the carboxyl group occurs in an aliphatic side-chain of an alkyl benzene. The first group or class is naturally more nearly related to benzoic acid than the second group.

Alkyl Benzoic Acids.—*Toluic acids* or *monomethyl benzoic acids*, $CH_3.C_6H_4.CO_2H$, are isomeric with *a-toluic acid* or *phenylacetic acid* (p. 196). They are produced when the three xylenes are boiled for some time with dilute nitric acid, and from brom- and

iod-toluene, by the nucleus-synthetic methods 5 and 6, as well as from the three toluidines according to method 10.

o-Toluic acid can also be obtained by the reduction of phthalide with hydriodic acid (B. 20, R. 378), as well as by rupturing the ring of 1,3-naphthalene derivatives, like 1,3-dioxynaphthalene, 1,3-naphthalene disulphonic acid, 1,3-naphthol sulphonic acid upon fusing them with caustic alkali (B. 29, 1611). p-Toluic acid is formed on boiling cymene (p. 56) with dilute nitric acid.

o-Toluic acid melts at 102°.
m-Toluic acid " " 110° and boils at 263°.
p-Toluic acid " " 180° " " 275°.

Ethyl Benzoic Acids, $C_2H_5 . C_6H_4 . CO . OH$.—The three isomerides are known. The o-acid results in the reduction of o-acetophenone carboxylic acid, of methyl phthalide (B. 29, 2533), and of phthalyl acetic acid, $C_6H_4\begin{cases} C = CHCO_2H \\ \quad >O \\ CO \end{cases}$, with hydriodic acid (B. 10, 2206), and in that of the chlorvinylbenzoic acids with sodium amalgam (B. 27, 2761).

o-, m-, and p-Ethyl Benzoic Acids melt at 68°, 47°, and 112° (B. 21, 2830; A. 216, 218) respectively.

Dimethyl Benzoic Acids, $(CH_3)_2C_6H_3CO_2H$.—Mesitylenic acid is the most important member of this group. It is formed when mesitylene, symmetrical or [1,3,5]-trimethyl benzene (p. 55), is oxidized with dilute nitric acid. Isoxylene or m-xylene is obtained when this acid is distilled with lime. These reactions are the basis of the evidence that isoxylene (p. 54) and its oxidation products, m-toluic acid and isophthalic acid, are m-disubstitution products of benzene (p. 37). Further oxidation of mesitylenic acid leads to *uvitic acid* and *trimesic acid.*

1,2-Dimethyl-3-benzoic Acid, α-Hemellitic Acid, melts at 144° (B. 19, 2518).
1,2-Dimethyl-4-benzoic Acid, p-Xylic Acid, . . " 163° (B. 17, 2374).
1,3-Dimethyl-2-benzoic Acid, ... " 98° (B. 11, 21).
1,3-Dimethyl-4-benzoic Acid, ... " 126° (B. 12, 1968).
1,3-Dimethyl-5-benzoic Acid, **Mesitylenic Acid,** " 166° (A. 141, 144).
1,4-Dimethyl-2-benzoic Acid, Isoxylic Acid, . . " 132°; boils at 268° (A. 244, 54).

Propyl Benzoic Acids, $C_3H_7 . C_6H_4CO_2H$.—o- and p-n-Propyl and p-isopropyl benzoic acids are known. p-Isopropyl benzoic acid, or ***cumic acid,*** the oxidation product of cuminic alcohol (p. 184) (B. 11, 1790), is deserving of the most note. Cumic acid is further produced by the oxidation of cymene (p. 56) in the animal organism, as well as by the rearrangement of *nopic acid* which results from the oxidation of turpentine oil (B. 29, 1927). Chromic acid oxidizes cumic acid to terephthalic acid, and potassium permanganate converts it into p-oxyisopropyl benzoic acid and p-acetyl benzoic acid:

o,n-Propylbenzoic acid melts at 58° (B. 11, 1014).
p,n-Propylbenzoic acid melts at 138° (B. 21, 2231).
o-Isopropylbenzoic acid melts at 51° (A. 248, 63).

Cumic Acid, p-Isopropyl Benzoic Acid, melts at 117° (A. 219, 279; B. 20, 860).

Trimethyl Benzoic Acids.—Five are known. Durylic acid is obtained from durene, and α-, β-, and γ-isodurylic acids from isodurene (B. 27, 3446), upon oxidation with

dilute nitric acid. β-Isodurylic acid or mesitylene carboxylic acid can also be formed from acetyl mesitylene (p. 190) (B. **25**, 503):

1,2,3-Trimethyl-4-benzoic Acid,	Prehnitylic Acid,	melts at	167°.
1,2,3-Trimethyl-5-benzoic Acid,	α-Isodurylic Acid,	"	215°.
1,2,4-Trimethyl-5-benzoic Acid,	Durylic Acid, .	"	150°.
1,2,4-Trimethyl-6-benzoic Acid,	γ-Isodurylic Acid,	"	127°.
1,3,5-Mesitylene Carboxylic Acid,	β-Isodurylic Acid,	"	152°.

Tetramethyl Benzoic Acids.—Several are known: 1,2,3,4-Tetramethyl-5-benzoic acid, melting at 165°, is the oxidation product of pentamethyl benzene (B. **20**, 3287); 1,2,3,5-*Tetramethyl-6-benzoic acid*, durene carboxylic acid (B. **29**, 2569); 2,3,5,6-*Tetramethyl Benzoic Acid* melts at 127° (B. **29**, R. 233).

Pentamethyl Benzoic Acid, $(CH_3)_5 . C_6 . CO_2H$, melting at 210°, is made according to method 8 (B. **22**, 1221).

Phenyl Fatty Acids.—The most important representatives of this group are phenylacetic acid or α-toluic acid, β-phenylpropionic acid or hydrocinnamic acid, and α-phenylpropionic acid or hydratropic acid. The synthesis and decomposition of the phenyl fatty acids can be realized in the same manner as the synthesis and decompositions of the fatty acids (I, 251). The general methods of formation 2, 3, 4, 10*b*, 11, 12, and 13 (pp. 191, 192) are particularly prominent in the formation of the phenyl fatty acids.

Phenyl-acetic Acid, *Alphatoluic Acid,* $C_6H_5 . CH_2 . CO_2H$, melts at 76° and boils at 262°. This acid is formed from toluene just as acetic acid is obtained from methane. Toluene is converted into benzyl chloride, and this into benzyl cyanide (method 10*b*, p. 192), which is then digested with sulphuric acid (B. **19**, 1950; **20**, 592):

$$CH_4 \longrightarrow CH_3Cl \longrightarrow CH_3CN \longrightarrow CH_3 . CO_2H.$$
$$C_6H_5 . CH_3 \longrightarrow C_6H_5CH_2Cl \longrightarrow C_6H_5 . CH_2CN \longrightarrow C_6H_5 . CH_2 . CO_2H.$$

It can also be obtained from phenyl chloracetic acid, $C_6H_5 . CHCl . CO_2H$ (B. **14**, 240), from phenyl glycollic acid or mandelic acid, $C_6H_5CH(OH) . CO_2H$, and phenylglyoxylic acid, $C_6H_5 . CO . CO_2H$, by reduction.

It is produced when phenylmalonic acid is heated (see method 12, p. 193), and it appears in the decay of albuminates (B. **12**, 649). It may be prepared, furthermore, from brombenzene, chloracetic ester, and copper (B. **2**, 738), and by heating acetophenone with yellow ammonium sulphide (B. **21**, 534). Chromic acid oxidizes it to benzoic acid. Chlorine, in the heat, converts it into phenylchloracetic acid, while in the cold the halogens replace the aromatic hydrogen.

Tolyl-acetic Acids, Alpha-xylic Acids, $C_6H_4<^{CH_3}_{CH_2 . CO_2H}$.—The three isomeric acids have been obtained from the three xylene bromides. The *ortho*-acid melts at 89°, the *meta* at 61°, and the *para* at 91° (B. **20**, 2051; **24**, 3965).

The esters of two acids, isomeric with phenyl- and tolyl-acetic acids, result from the action of diazo-acetic ester (I, 365) upon benzene and toluene. These acids have been called *pseudophenyl-acetic acid* (the *amide* melts at 141°) and *pseudotolyl-acetic acid.* The only product formed in any appreciable amount by the oxidation of pseudophenyl-acetic acid is terephthalic acid. The constitution of this body has never been explained. It has been assumed that it contains the residue =CH . COOH, attached to two carbon atoms of the nucleus (B. **29**, 106, 632).

I

Hydrocinnamic Acid, β-Phenylpropionic Acid, $C_6H_5 . CH_2 . CH_2 . CO_2H$, melting at 47° and boiling at 280°, is isomeric with α-phenylpropionic acid, the three alphaxylic acids, the three ethylbenzoic acids, and the six dimethylbenzoic acids. It is obtained: by the action of sodium amalgam upon cinnamic acid, or β-phenylacrylic acid, or hydriodic acid (B. **13**, 1680); from phenylethyl cyanide (A. **156**, 249); from benzyl acetoacetic ester (B. **10**, 758) and benzyl malonic ester (A. **204**, 176); also from benzyl acetic ester with sodium (A. **193**, 300) (see, further, methods 11, 12, and 13); and in the decay of albuminoid substances (B. **12**, 649). Chromic acid oxidizes it to benzoic acid.

The aliphatic haloid hydrocinnamic acids, readily obtained by the addition of haloid acids and halogens to cinnamic acid, will be described after phenyllactic and phenylglyceric acids.

Hydratropic Acid, α-Phenyl-propionic Acid, $C_6H_5CH(CH_3) . CO_2H$, boiling at 265°, is an oil, volatile in aqueous vapor. It results from the reduction of atropic acid or α-phenylacrylic acid, $C_6H_5 - C(=CH_2) . CO_2H$, and in the action of hydriodic acid upon the prussic acid addition product of acetophenone—the nitrile of atrolactinic acid (A. **250**, 135).

Higher homologues of these acids are usually made according to the following reactions: (1) By reduction of homologous cinnamic acids (see these), which can be readily prepared by Perkins' reaction from the aromatic aldehydes. (2) By the reduction of homologous mandelic acids, obtained from homologous phenylglyoxylic acids. The latter result upon oxidizing homologous acetyl benzenes with potassium permanganate. (3) From alkylized benzyl cyanides, which are produced by the action of alkylogens upon sodium benzyl cyanide.

γ-Phenyl-butyric Acid, $C_6H_5 . CH_2 . CH_2 . CH_2 . COOH$, melting at 51.7°, is formed by the reduction of phenylbutyrolactone. *δ-Phenyl-valeric Acid*, $C_6H_5(CH_2)_4COOH$, melting at 59°, results from the reduction of phenyl coumalin (see this) with hydriodic acid (B. **29**, 1675, R. 14).

DERIVATIVES OF THE AROMATIC MONOCARBOXYLIC ACIDS.

The derivatives of benzoic acid and its homologues arrange themselves into two groups. The first group comprises those compounds resulting from the alteration of the carboxyl group (see Acetic Acid, 1, 222, 223), and the second group the aromatic substitution products with the exception of the phenol monocarboxylic acids. The first group divides itself into A, the benzoyl compounds; B, the benzenyl compounds and the derivatives of orthobenzoic acid. The chemistry of no single carboxylic acid has been so richly developed as that of benzoic acid.

A. BENZOYL COMPOUNDS.

1. **Esters of the Monobasic Aromatic Acids** (1, 254).—The benzoic esters of the alcohols and phenols can be prepared like the acetic esters. Like the latter, they are frequently employed in determining the number of alcoholic hydroxyl groups present in a compound. They are made (1) by the action of hydrochloric acid upon an alcoholic solution of benzoic acid; (2) by the action of benzoyl chloride or benzoic anhydride upon alcohols, alcoholates, phenols, and phenolates; (3) by the action of alkylogens upon salts,

usually the silver salts. In carrying out the second reaction it is advisable to gradually add sodium hydroxide, and shake the alkaline, aqueous solution of the alcohols with benzoyl chloride until there is a permanent alkaline reaction (Baumann, B. **19**, 3218). In this manner, also, the benzoyl ethers of the polyalcohols, the polyoxyaldehydes,—*e. g.*, of the glucoses,—have been obtained, and nearly all have been completely benzoylated (B. **22**, R. 668).

Methyl Benzoic Ester boils at 199°. The *ethyl ester* boils at 213°; the n-*propyl ester* at 229°; the n-*butyl ester* at 247°. *Glycol Dibenzoate* melts at 73° (B. **23**, 2498). *Glycerol Tribenzoate* melts at 76° (B. **24**, 779). *Erythrol Tetrabenzoate* melts at 187°. *Mannitol Hexabenzoate* melts at 124°. *Glucose Pentabenzoate* melts at 179°.

Benzoyl Glycollic Acid, $C_6H_5CO.OCH_2.CO_2H$, consists of large prisms. It results when nitrous acid acts upon hippuric acid. *Phenyl Benzoic Ester* melts at 71° and boils at 314° (A. **210**, 255; B. **24**, 3685). The *benzyl ester* melts at 20° and boils at 323° (B. **20**, 647). It occurs in Peru balsam (A. **152**, 130). See pp. 147, 160, and 163 for the benzoyl compounds of the homologous phenols.

The 2,6- and 2,4,6-substituted benzoic acids, like mesitylene carboxylic acid, 2,6-dibrom-, and 2,4,6-tribrom-, 2,4,6 trinitrobenzoic acids, etc., are not converted into esters when treated with alcohol and hydrochloric acid. The acids not esterified in this way are quite readily changed to esters by the interaction of alkylogens and the silver salts (B. **28**, 1468; **29**, 1399; compare **29**, 2301).

2. **Aromatic Acid Haloids or Haloid Anhydrides of the Aromatic Acids** (1, 257).—The methods pursued in the preparation of these bodies are similar to those employed for the corresponding fatty derivatives (1, 257).

Benzoyl Chloride, $C_6H_5.COCl$, melting at −1° and boiling at 198°, is isomeric with the chlorinated benzaldehydes, $Cl.C_6H_4.CHO$. It is a liquid with penetrating odor. It is formed from benzoic acid, phosphorus pentoxide, and hydrochloric acid (B. **2**, 80); from benzaldehyde and chlorine; from sodium benzoate and phosphorus oxychloride; and from benzoic acid and phosphorus pentachloride. The action of phosgene and aluminium chloride upon benzene hydrocarbons, and of anhydrous oxalic acid upon benzotrichloride (A. **226**, 20), are only applicable in the preparation of the chlorides of benzene carboxylic acids.

The history of benzoyl chloride, the first discovered chloride of a carboxylic acid, was given in connection with the fatty acid chlorides (1, 257). Benzoyl chloride is readily accessible and very reactive; it is therefore one of the most frequently used compounds in various reactions.

o- and m-*Toluyl Chlorides* boil at 211° and 218° respectively. *Phenyl Acetyl Chloride*, $C_6H_5.CH_2.COCl$, boils at 102° (17 mm.) (B. **20**, 1389).

Benzoyl Bromide, $C_6H_5.COBr$, melting about 0° and boiling at 218°, results from the action of phosphorus tribromide upon benzoic acid (B. **14**, 2473). *Benzoyl iodide*, consisting of crystalline leaflets, is produced when potassium iodide acts upon benzoyl chloride (B. **3**, 266). *Benzoyl fluoride*, from benzoyl chloride and AgF, boils at 145°.

So far as concerns properties, *benzoyl azimide* or *benzoyl nitride*, to be treated later in connection with benzoyl hydrazine, attaches itself to the halogen anhydrides of benzoic acid.

3. **Acid Anhydrides** (1, 259).—*Benzoic Anhydride*, $(C_6H_5.CO)_2O$, melting at 42° and boiling at 360°, is obtained from benzoyl chloride and sodium benzoate or silver benzoate; from benzoyl chloride and benzotrichloride upon digesting them with anhydrous oxalic acid; from benzoyl chloride by means of lead nitrate (B. **17**, 1282) or sodium nitrite (B. **24**, R. 371), and by the action of concentrated sulphuric acid upon benzotrichloride (B. **12**, 1495).

Aceto-benzoic Anhydride breaks down, when heated, into acetic anhydride and benzoic anhydride (B. **20**, 3189).

o-*Toluic Anhydride* melts at 37°. *Phenyl-acetic anhydride*, $(C_6H_5.CH_2.CO)_2O$, melts at 72° (B. **20**, 1391).

4. **Acid Peroxides** (1, 261).—*Benzoyl Peroxide*, $(C_6H_5CO)_2O_2$, melts at 103° and deflagrates when heated. It is formed from benzoyl chloride and barium peroxide, or from benzoyl chloride, hydrogen peroxide, and sodium hydrate (B. **27**, 1511; **29**, 1727), as well as from benzaldehyde, acetic anhydride, and sand, upon exposure to the air (B. **27**, 1960).

5. **Thioacids** (1, 261).—**Thiobenzoic Acid,** $C_6H_5.CO.SH$, melts at 24°, and results when benzoyl chloride acts upon alcoholic potassium sulphide. When the ethereal solution of thiobenzoic acid is exposed to the air (A. 115, 27) the acid rapidly changes to *Benzoyl disulphide*, $(C_6H_5O)_2S_2$, melting at 138°. *Benzoyl sulphide*, $(C_6H_5O)_2S$, melts at 48°, and is obtained when benzoyl chloride acts upon thiobenzoic acid (Z. f. Ch. (1868), 357).

Thionbenzoic Acid, C_6H_5CSOH (A. 140, 236).

Dithiobenzoic Acid, $C_6H_5.CS.SH$, a heavy, dark violet-red oil, is obtained when $C_6H_5.CCl_3$ is boiled with alcoholic potassium sulphide (A. 140, 240).

6. **Acid Amides** (1, 262).—The methods of formation and the deportment of the acid amides have been sufficiently considered in connection with the fatty acid amides. Attention was also called to the fact that the amides of the carboxylic acids could have two constitution formulas. Thus, benzamide has two formulas:

$$\text{I. } C_6H_5C\langle^{NH_2}_{O} \quad \text{and} \quad \text{II. } C_6H_5C\langle^{NH}_{OH}.$$

The imido-ethers are derived from the second formula (see silver benzamide). In addition to the methods mentioned under the amides of the fatty acids must be added, in connection with the amides of the benzene carboxylic acids, their formation through the action of aluminium chloride upon aromatic hydrocarbons and urea chlorides (p. 192).

Benzamide, $C_6H_5.CO.NH_2$, melting at 130° and boiling at 288°, results (1) when benzoyl chloride is acted upon by gaseous or aqueous ammonia, or by ammonium carbonate (see tribenzamide); (2) from benzoic ester and ammonia; (3) by heating benzoic acid and ammonium thiocyanate to 170° (A. 244, 50). It crystallizes in pearly leaflets, melts at 130°, and boils near 288°. It is readily soluble in hot water, alcohol, and ether.

Sodium Benzamide, $C_6H_5CONHNa$ or $C_6H_5C(:NH)ONa$, results from the action of metallic sodium upon benzamide dissolved in benzene (B. 23, 3038).

Silver Benzamide, $C_6H_5.CO.NHAg$ or $C_6H_5.C(:NH).O.Ag$, obtained by precipitating the aqueous solution of benzamide and silver nitrate with a calculated amount of sodium hydroxide, is a white crystalline powder. When digested with ethyl iodide it yields benzimido-ethyl ether (B. 23, 1550); a behavior arguing for the II-formula for the silver salt.

Dibenzamide, $(C_6H_5CO)_2NH$, melting at 148°, is obtained from benzonitrile with concentrated sulphuric acid, or from benzoyl chloride and benzonitrile with aluminium chloride. When distilled under a pressure of 15 mm. dibenzamide breaks down into benzonitrile and benzoic acid (B. 21, 2389). *Sodium dibenzamide*, $(C_6H_5CO)_2NNa$, is a shining, white powder. It is formed when sodium acts upon dibenzamide dissolved in xylene.

Tribenzamide, $(C_6H_5CO)_3N$, melting at 202°, results in the action of benzoyl chloride in ethereal solution upon sodium dibenzamide, and together with benzamide and dibenzamide when benzoyl chloride acts upon ammonium carbonate (B. 25, 3120).

Benzoyl Chlorimide, $C_6H_5CONHCl$, melts at 113°. *Benzoyl Bromimide*, $C_6H_5.CONHBr$, melts with decomposition at 170°. *Methyl* and *Dimethyl Benzamide*, $C_6H_5CON(CH_3)_2$, melt at 78° and 41°.

We get **Benzanilide,** $C_6H_5.CO.NH.C_6H_5$, **Phenyl-benzamide,** on mixing aniline and benzoyl chloride. It can also be made by the action of aluminium chloride (p. 192) upon benzene and carbanile, and upon heating benzophenoxime, $(C_6H_5)_2C:N.OH$, with concentrated sulphuric acid, acetyl chloride, or glacial acetic acid containing hydrochloric acid, to 100°, or with glacial acetic acid alone to 180° (B. 20, 2581).

When benzanilide is boiled with sulphur it becomes *benzenylamidothiophenol* or μ-phenylbenzothiazole (p. 153). o-, m-, and p-*Benzoyl Toluides*, $C_6H_5CONH.C_6H_4CH_3$, melt at 131°, 125°, and 158°.

Diphenylbenzamide, $C_6H_5CO \cdot N(C_6H_5)_2$, melting at 177°, results from diphenylamine and benzoyl chloride, as well as from diphenylurea chloride, benzene and aluminium chloride (B. **20**, 2119).

Benzoyl Benzylamine, $C_6H_5CO \cdot NH \cdot CH_2 \cdot C_6H_5$, melts at 105° (B. **26**, 2273).

Methylene-dibenzamide, *hipparaffin*, $CH_2(NH \cdot CO \cdot C_6H_5)_2$, melting at 221°, is obtained in the oxidation of hippuric acid with PbO_2 and dilute sulphuric or dilute nitric acid, and results from formaldehyde, benzonitrile, and hydrochloric acid (B. **25**, 311).

Ethidene Dibenzamide, $CH_3 \cdot CH(NHCOC_6H_5)_2$, melts at 204° (B. **7**, 159).

Ethylene Dibenzamide, $C_6H_5CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO \cdot C_6H_5$, melting at 249°, when heated alone or with hydrochloric acid yields ethylene benzenylamidine, benzoic acid splitting off at the same time (B. **21**, 2334).

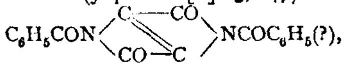
Hippuric Aldehyde, $C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot COH$ (B. **27**, 3093). Its acetal is formed from amido-acetal (I, 316).

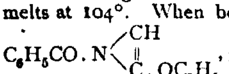
Hippuric Acid, Benzoyl glycocoll, $CH_2<^{NH \cdot CO \cdot C_6H_5}_{CO_2H}$, melting at 187°, decomposes at 240° into benzoic acid, benzonitrile, and prussic acid. It occurs in considerable amount in the urine of herbivorous animals, in that of the cow and horse (ἵππος, horse, οὖρον, urine), and in minute quantities in that of man. Benzoic acid, cinnamic acid, toluene, and other aromatic substances, when taken internally, are eliminated as hippuric acid. It can be obtained artificially (1) by heating benzamide with monochloracetic acid; (2) by the action of benzoyl chloride on silver glycocollide (B. **15**, 2740), or (3) by adding sodium hydroxide to glycocoll and shaking with benzoyl chloride (B. **19**, R. 307), and (4) by heating benzoic anhydride with glycocoll (B. **17**, 1662).

History.—Liebig, in 1829, recognized that hippuric acid was a different body from benzoic acid, and to indicate its origin named it hippuric acid. In 1839 he established its constitution. Dessaignes (1846) showed how upon boiling with strong alkalies or acids it was resolved into glycocoll and benzoic acid (J. pr. Ch. [1] 37, 244). In 1848 Strecker converted the acid by means of nitrous acid into benzoyl glycollic acid (A. **68**, 54), and in 1853 Dessaignes synthesized hippuric acid from benzoyl chloride and zinc glycocollide (A. **87**, 325).

Hippuric acid crystallizes in rhombic prisms, and dissolves in 600 parts cold, and readily in hot water and alcohol. Boiling acids or alkalies decompose hippuric acid into benzoic acid and glycocoll.

Compare *hipparaffin* (above), *benzoylglycollic acid* (p. 198), for other transformations of hippuric acid. Hippuric acid condenses with benzaldehyde, sodium acetate and acetic anhydride to benzoylamidocinnamic lactimide (A. **275**, 3).

Silver salt, $C_9H_8AgNO_3$. The *ethyl ester* melts at 60° (J. pr. Ch. [2] **15**, 247). It is converted by PCl_5 (2 mols.) into *hippuroflavin*,  consisting of citron-yellow crystals (B. **21**, 3321; **26**, 2324). Benzaldehyde and sodium acetate change it to *benzoylamidocinnamic ester* (A. **275**, 12). The *phenyl ester* melts at 104°. When boiled with $POCl_3$ it passes into *anhydrohippuric phenyl ester*,

 , melting at 42° (B. **26**, 2641).

Hippuryl-hydrazine, $C_6H_5CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot NH_2$, melting at 162°, is formed from ethyl hippuric ester and hydrazine. Compare *hippuryl-phenyl-buzylene* (p. 131) and *hippurazide* (p. 201) (B. **29**, R. 181).

7. **Acid Hydrazides** (I, 228, 405; II, 125). *Benzoyl Hydrazine*, $C_6H_5CO \cdot NHNH_2$,

melting at 112°, is obtained from benzoic ester and hydrazine. When there is an excess of the ester, sym. *Dibenzoyl Hydrazine*, $(C_6H_5CO : NH)_2$, is formed. This melts at 233° (B. 27, R. 899) (see also benzoylazide, below). *Benzoyl Phenylhydrazine*, melting at 168° (B. 19, 1203), is converted by mercuric oxide into *benzoyl diazobenzene*, $C_6H_5 \cdot CON_2C_6H_5$. This yields an addition product with hydrochloric acid, but it rearranges itself to o-*chlorphenylbenzoylhydrazine* (B. 30, 319):

$$C_6H_5CONH . NCl . C_6H_5 \longrightarrow C_6H_5CONHNH[1]C_6H_4[2]Cl.$$

Unsym. *Benzoyl-phenylhydrazine* melts at 70° (B. 26, 945, R. 816). *Dibenzoyl-phenylhydrazine*, $C_6H_5 . CO . N(C_6H_5) . NHCO . C_6H_5$, melts at 177°.

8. **Acidylazides.—Benzoylazide**, *benzoyl nitride*, azimide, $C_6H_5CON\!<\!\overset{N}{\underset{N}{\|}}$, melting at 20°, is formed when sodium nitrite and acetic acid act upon benzoyl hydrazine (B. 23, 3023). Its odor is intensely like that of benzoyl chloride; it volatilizes in part with aqueous vapor without decomposition, and explodes with slight detonation upon the application of heat. It is insoluble in water, very soluble in ether, and rather readily soluble in alcohol. It reacts neutral. It breaks down, on boiling with alkalies, into benzoic acid and potassium azoimide (B. 23, 3029). Boiling alcohol changes it to phenylurethane, $C_6H_5NH . CO . OC_2H_5$, and nitrogen. Carbanilide and nitrogen result when it is boiled with water. Bromine converts it into nitrogen and a carbanile brom-addition product (J. pr. Ch. [2] 52, 215). The substituted benzoylazides behave similarly. o-, m-, and p-*Nitrobenzazides* melt at 36°, 68°, and 69°. The azides can also be obtained by the action of salts of diazo-benzene upon the acid hydrazides. Acidylated semicarbazides are produced on boiling the acid azides with the acid hydrazides (B. 29, R. 981) (p. 86):

$$C_6H_5CON_3 + C_6H_5CONHNH_2 = N_2 + C_6H_5NHCONH . NHCOC_6H_5.$$

Hippurazide, $C_6H_5CO . NH . CH_2 . CO . N_3$, melting at 98°, results when sodium nitrite and acetic acid act upon hippuryl hydrazine. It is decomposed by mineral acids, alkalies, ammonia, and amines, with the elimination of *hydrazoic acid*. When boiled with alcohols and with water N_2 is evolved, and there result *Hippenyl urethane*, $C_6H_5 \cdot CONHCH_2NHCOOR$, and *Dihippenylurea*, $(C_6H_5CONHCH_2NH)_2CO$ (B. 29, R. 183).

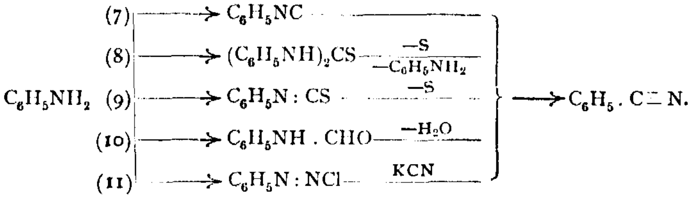
9. **Nitriles of the Aromatic Monocarboxylic Acids.**—The aromatic nitriles are connected by numerous reactions with the principal classes of the aromatic derivatives. They are produced, like the nitriles of the fatty acids (1, 266), (1) from the corresponding ammonium salts; (2) from the corresponding acid amides by the withdrawal of water with P_2O_5, PCl_5, and $SOCl_2$ (B. 26, R. 401); (3) by the action of bromine and caustic alkali upon the primary phenylalkylamines; (4) from the aldoximes by the action of acetyl chloride or acetic anhydride. There is also (5) the method of distilling aromatic monocarboxylic acids with potassium sulphocyanide, or, better, with lead sulphocyanide (B. 17, 1766):

$$2C_6H_5 . CO_2H + (CNS)_2Pb = 2C_6H_5CN + 2CO_2 + PbS + H_2S.$$

Nucleus-synthetic Methods.—(6) The direct replacement of the halogens in the benzene hydrocarbons by the cyanogen group is of exceptional occurrence—*e. g.*, when chlor- and brom-benzene are conducted over strongly ignited potassium ferrocyanide, or when benzene iodide is heated to 300° with silver cyanide, the product being cyanbenzene.

However, the phenyl carbinol chlorides—*e. g.*, $C_6H_5CH_2Cl$—are as readily transposed as the alkylogens into nitriles of the phenyl-fatty acids by means of potassium cyanide.

The nitriles are also intimately related to the anilines, sulphonic acids, and phenols. Thus, aniline yields (7) phenylcarbylamine, which, upon the application of heat, is rearranged into the isomeric nitrile. They are also produced (8) on heating the diphenyl thioureas with zinc-dust; (9) by desulphurizing the phenyl mustard oils with copper; (10) by distilling the formanilides with concentrated hydrochloric acid or with zinc-dust (B. **17**, 73); (11) by decomposing diazobenzene chloride with potassium cyanide and copper sulphate.



See p. 38 for the theoretical value of method 11.

(12) By distilling the alkali benzene sulphonates with potassium cyanide or yellow prussiate of potash; (13) the distillation of the triphenyl phosphates with potassium cyanide or ferrocyanide; (14) alkyl benzylcyanides are formed by the interaction of sodium benzyl cyanide and alkylogens, $C_6H_5.CHNa.CN + C_2H_5I = C_6H_5CH(C_2H_5)CN$ (p. 203); (15) the hydrogen atoms of the benzenes are directly replaced by the cyanogen group, if cyanogen gas be conducted into the boiling hydrocarbon mixed with aluminium chloride (B. **29**, R. 185). Certain nitriles of phenyl-fatty acids occur in the different cresses.

Properties and Deportment.—The benzonitriles are indifferent, agreeably smelling liquids, or solids with low melting points. Their reactions are very numerous, but mention may be made that boiling alkalies or acids convert them into the corresponding aromatic acids, while nascent hydrogen, best from alcohol and sodium, changes them to primary amines. They yield *amide iodides* with hydriodic acid.

They combine with alcohols and HCl to form imido-ethers, with anilines to *amidines*, and with hydroxylamine to *amidoximes*.

Benzonitrile, *Cyanbenzene*, $C_6H_5.CN$, boiling at 191°, with sp. gr. 1.023 (0°), is isomeric with phenyl carbylamine (p. 83), and is best obtained from benzene sulphonic acid by method 12, or from benzoic acid by method 5. It is an oil with an odor resembling that of oil of bitter almonds.

When it is dissolved in fuming sulphuric acid or boiled with sodium, benzonitrile polymerizes to *cyanphenine* (see this), $C_3N_3(C_6H_5)_3$. Upon nitration the product is almost exclusively m-nitrobenzonitrile (p. 69). For other transpositions see benzimido-ethers and thiobenzamide.

Alphylcyanides: o-, m-, and p-*Tolunitriles*, cyantoluenes, $CH_3.C_6H_4CN$, boil at 203°, 213°, and, 218°. The p-body melts at 29°. p-*Xylonitrile* boils at 231° (B. **18**, 1712)? 1,3-*Xylo-4-nitrile* melts at 24° and boils at 222° (B. **21**, 3082). *Cumonitrile*, $(CH_3)_2.CH[4]C_6H_4[1]CN$, boils at 244°.

Nitriles of Phenyl-fatty Acids: **Benzyl Cyanide,** *Phenylacetonitrile,* $C_6H_5 . CH_2CN$, boiling at 232°, with sp. gr. 1.014 (18°), is isomeric with the three tolunitriles. It occurs in the ethereal oil of several cresses (*Tropæolum majus* and *Lepidium sativum* (B. 7, 1293). It is artificially prepared from benzyl chloride with potassium cyanide. It yields toluic acid by saponification; by reduction β-phenylethylamine (p. 179) is the product, and upon nitration it is chiefly p-nitrobenzyl cyanide which results.

As in acetoacetic ester and malonic ester, the hydrogen of the CH_2 group, combined with the negative groups C_6H_5 and CN, is very readily replaced. Thus, sodium ethylate produces the mono-sodium derivative, which may be transposed by alkylogens to alkyl benzyl cyanides (see method 14, p. 202) (B. 21, 1291, R. 197; 22, 1238; 23, 2070). Nitrous acid, acting upon a sodium ethylate solution of benzyl cyanide, produces isonitrosobenzyl cyanide (see phenylglyoxalic acid). Sodium ethylate, acting upon benzyl cyanide and benzaldehyde, produces α-phenyl-cinnamic nitrile, $C_6H_5 . C(CN) : CH . C_6H_5$ (B. 22, R. 199).

Methyl Benzyl Cyanides, Tolylacetonitriles, $CH_3 . C_6H_4 . CH_2 . CN$. The o-body boils at 244°, the meta-body at 241°, while the p-compound melts at 18° and boils at 243° (B. 18, 1281; 21, 1331).

β-Phenylpropionitrile, hydrocinnamic nitrile, $C_6H_5CH_2CH_2CN$, boiling at 261° (corr.), occurs in the ethereal oil of spring-cress, *Nasturtium officinale* (B. 7, 520; B. 26, 1971).

α-Phenylpropionitrile, hydratropic nitrile, $C_6H_5CH(CH_3)CN$, boils at 231° (A. 250, 123, 137).

B. BENZENYL COMPOUNDS.

In addition to the benzonitriles, the classes of bodies from 10 to 26 (p. 209) arrange themselves with the benzenyl derivatives.

10. **Amid-haloids.** 11. **Imide Chlorides.** 12. **Phenylhydrazide Imide Chlorides** (1, 268).

Benzamide Chloride, $C_6H_5CCl_2 . NH_2$ (?), results when hydrochloric acid gas is conducted into an ethereal solution of benzonitrile (B. 10, 1891). *Benzamide Bromide,* phenyldibromformamide, $C_6H_5CBr_2NH_2$, melts at 70° (A. 149, 307). *Benzamide Iodide,* phenyldi-iod-formamide, $C_6H_5CI_2NH_2$, melts with decomposition (B. 25, 2536) at 140°. It is produced when benzonitrile is poured into concentrated aqueous hydriodic acid. Ammonia bases reconvert it into benzoic acid.

Dimethyl Benzamide Chloride, $C_6H_5 . CCl_2 . N(CH_3)_2$, from the amide and phosgene, melts at 36°.

Benzanilid-imide Chloride, $C_6H_5CCl : N . C_6H_5$, melting at 40° and boiling at 310°, is produced when PCl_5 acts upon benzanilide (Wallach, A. 184, 79), or upon benzophenone oxime, $(C_6H_5)_2C = N . OH$, by an intramolecular atomic rearrangement of the chloride, $(C_6H_5)_2C = NCl$. Water or alcohol will decompose it into hydrochloric acid and benzanilide. For other transpositions of benzanilide-imide chloride, compare thiobenzanilide, etc.

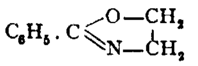
When benzanilide-imide chloride acts upon sodium acetoacetic ester the products are *anil-benzenyl*-compounds, β-ketonic acid derivatives, which change to phenyl-quinoline carboxylic acids upon the application of heat.

Benzphenylhydrazid-imide chloride, $C_6H_5CCl : N . NH . C_6H_5$, melting at 131°, is formed when alcohol acts upon the reaction product of PCl_5 and sym. benzoylphenylhydrazine, $C_6H_5 . CCl : N . N(C_6H_5)POCl_2$ (B. 27, 2122).

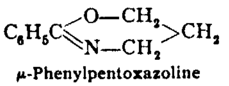
13. **Imido-ethers of the Aromatic Acids** (1, 269). The *imido-ethers* (their HCl-salts) result from the action of HCl upon a mixture of a nitrile with an alcohol (Pinner, B. 16, 1654; 21, 2650; 23, 2917).

Water decomposes the HCl-imido-ethers into acid esters and ammonium chloride.

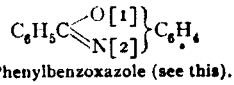
The following bodies should be viewed as imido-ethers of aromatic carboxylic acids:



μ-Phenyloxazoline



μ-Phenylpentoxazoline



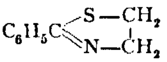
μ-Phenylbenzoxazole (see this).

Benzimido-ethyl Ether, $C_6H_5 . C(NH) . O . C_2H_5$, is a thick oil, formed by the action of ethyl iodide upon silver benzamide. Its hydrochloric acid salt decomposes at 120° into benzamide and ethyl chloride. The free ether decomposes when heated or upon standing into alcohol and cyanphenine. Ammonia converts it into *benzamidine* (see this), hydroxylamine into *benzamidoxime* (see this), and hydrazine into *benzenylhydrazidine*.

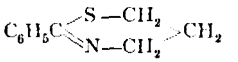
14. **Thiamides of the Aromatic Acids.**—*Thiobenzamide*, $C_6H_5 . CSNH_2$ or $C_6H_5C(SH)NH$, melting at 116°, results on conducting hydrogen sulphide into an alcoholic solution of benzonitrile mixed with ammonia (B. **23**, 158), and when benzylamine is heated to 280° with sulphur (A. **259**, 304). Zinc and hydrochloric acid convert it into benzylamine (p. 179), iodine into dibenzenylazosulphime (see this), $C_6H_5C{\lt}^{N—S}_{N=}{\gt}C . C_6H_5$ (B. **25**, 1588), ethylene bromide into μ-phenylthiazoline (see below), trimethylene bromide into μ-phenylpenthiazoline (see imido ethers), and ethylene-diamine into benzenylethylene diamine (see this), $C_6H_5C{\lt}^{NH—CH_2}_{N——CH_2}$ (B. **25**, 2134).

Thiobenzanilide, $C_6H_5 . CSNH . C_6H_5$, melting at 98°, consists of yellow plates or prisms. It is formed (1) when H_2S acts upon benzenylphenylamidine at 100°; (2) by the action of CS_2 at 110°, hydrosulphocyanic acid being simultaneously produced (A. **192**, 29); (3) when H_2S acts upon benzanilide chloride; (4) when P_2S_5 acts upon benzamide; (5) from the interaction of phenyl mustard oil, benzene, and aluminium chloride (B. **25**, 3525). It is changed to benzenylamidothiophenol (p. 157) by heat or oxidation.

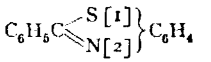
15. **Imidothio-ethers of the Aromatic Carboxylic Acids** are obtained as hydrochlorides from nitriles, mercaptans, and hydrochloric acid (compare imido-ethers). The following compounds must be considered as cyclic imidothio-ethers of benzoic acid:



μ-Phenylthiazoline



μ-Phenylpenthiazoline

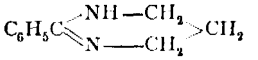


μ-Phenylbenzothiazole (see this).

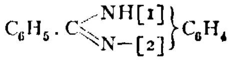
Benzimidothio-ethyl Ether, $C_6H_5C(NH)S . C_2H_5$, is an oil. It readily resolves itself into benzonitrile and mercaptan (A. **197**, 348).

16. **Amidines** of aromatic monocarboxylic acids (1, 270) are obtained from nitriles, imido-ethers, imide chlorides, and thioamides by means of ammonia and ammonium bases. The cyclic amidines correspond to the cyclic imido-ethers and imidothioethers:

μ-Phenylglyoxalidine
Ethylene Benzamidine



m-Phenyltetrahydropyrimidine
Trimethylene Benzamidine



μ-Phenylbenzimide-azole (see this).

Benzamidine,* *Benzenylamidine*, $C_6H_5 . C{\lt}^{NH}_{NH_2}$, melting at 75–80°, is formed from its *hydrochloride*, $C_7H_8N_2 . HCl + 2H_2O$, consisting of vitreous crystals, melting at 72°, which anhydrous become liquid at 169° (A. **265**, 130).

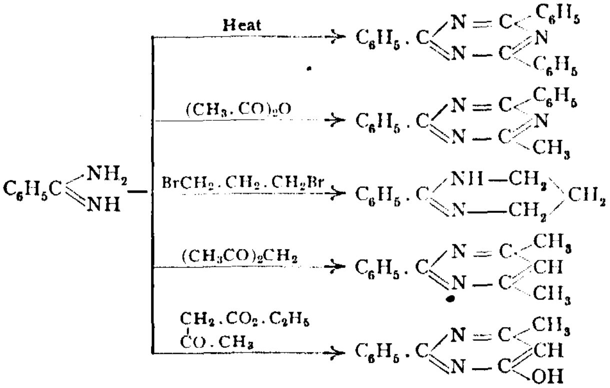
Silver salt, $C_6H_5 . C(=NAg)NH_2$. Benzamidine is a stronger base than ammonia. Hydroxylamine converts it, by an exchange of the NH-group for the N(OH)-group, into an amidoxime. Benzamidine gives with diazobenzene: *benzamidinediazobenzene* (see below); with benzaldehyde: *benzalbenzamidine*, melting at 175°; with phenylisocyanide: *benzenyldiphenyldiureide*, $C_6H_5C(: N . CONHC_6H_5) . NHCO . NH . C_6H_5$, melting at 172°; with phenyl mustard oil: *benzamidine phenylthiurea*, $C_6H_5 . C(: NH) . NH . CS$. -

* "Die Imidoäther und ihre Derivate," Pinner, 1892, p. 152.

$NH.C_6H_5$, melting at 125°; with chlorcarbonic ester: *benzamidine urethane*, $C_6H_5.C(:NH).NHCO_2C_2H_5$, melting at 58°; heat converts it into *diphenyloxycyanidine*; with phosgene: *dibenzamidine urea*: $CO(NH.C(:NH).C_6H_5)_2$, melting at 289°, and *diphenyloxycyanidine*.

The action of nitrous acid upon benzamidine is very remarkable. The product is *benzenyldioxytetrazotic acid* (see below).

Benzamidine Hetero-ring Formations.—Benzamidine heated alone becomes *cyanphenine*; heated with acetic anhydride the product is *diphenylmethylcyanidine*; with trimethylene bromide: *trimethylenebenzamidine*, or *μ phenyltetrahydropyrimidine*; with acetyl acetone: *phenyldimethylpyrimidine*; with acetoacetic ester: *phenylmethyloxypyrimidine*:



Cyanphenine

Diphenylmethylcyanidine (B. 25, 1624)

Phenyltetrahydropyrimidine (B. 26, 2122)

Phenyldimethylpyrimidine

Phenylmethyloxypyrimidine.

Many other amidines besides benzamidine are known; also numerous alkyl-, phenyl-, and benzyl substitution products of the simple amidines. As may be gathered from the description of benzamidine, the amidines are unusually reactive bodies, whose investigation has contributed much to the chemistry of the nitrogen-carbon ring systems. *Furfuramidine* (see this) deports itself very much the same as benzamidine.

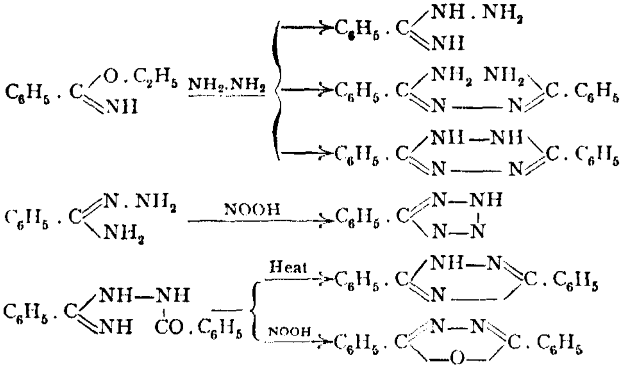
17. **Dioxytetrazotic Acids.**—Free *benzenyldioxytetrazotic acid*, $C_6H_5.C\begin{matrix}\diagup N=N.OH\\ \diagdown N-NO\end{matrix}$ (?), is not known. Its benzamidine salt, melting at 178°, is produced when nitrous acid acts upon benzamidine. Sodium amalgam reduces the potassium salt to *benzenyloxytetrazotic acid*, $C_7H_6N_4O + H_2O$, melting in anhydrous form at 175° with explosion, and *benzenyltetrazotic acid* (Lossen, A. 263, 73; 265, 129). These bodies belong to the class of heterocyclic tetrazoles or pyrrotriazoles.

18. **Hydrazidines or Amidrazones** of aromatic monocarboxylic acids. Several representatives of the aliphatic phenylhydrazidines were discussed in connection with phenylhydrazine. The simple aromatic hydrazidines result from the action of hydrazine upon the imido-ethers. The most thoroughly investigated is—

Benzenylhydrazidine, $C_6H_5.C\begin{matrix}\diagup NH.NH_2\\ \diagdown NH\end{matrix}$ or $C_6H_5.C\begin{matrix}\diagup N.NH_2\\ \diagdown NH_2\end{matrix}$. This compound cannot be obtained from its salts in a pure condition. Its *benzoyl* derivative, $C_6H_5C(:NH)NH.NH.CO.C_6H_5$, melts at 188°. It slowly parts with water, even at 120°, changing into c-diphenyltriazole, whereas nitrous acid converts it into dibenzenylisazoxime (see this).

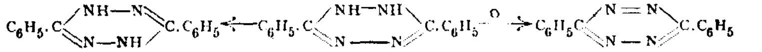
In addition to benzenylhydrazidine, produced in the interaction of hydrazine and benzimido-ether, there also result:

Dibenzenylhydrazidine, $C_6H_5.C(:NH).NH.NH(NH:)C.C_6H_5$ or $C_6H_5C(NH_2):N-N:(NH_2)C:C_6H_5$, melting at 202°, and *diphenyldihydrotetrazine* (see this). Nitrous acid changes benzenylhydrazidine into *phenyltetrazotic acid* (see this).



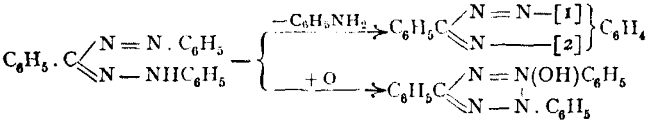
Benzenylhydrazidine
Dibenzenylhydrazidine
Diphenyldihydrotetrazine
c-Phenyltetrazotic Acid
c-Diphenyltriazole
Dibenzenylisazoxime.

Diphenyldihydrotetrazine is readily rearranged by acids into *isodiphenyldihydrotetrazine*. It oxidizes on exposure to the air to diphenyltetrazine (Pinner, B. 27, 3273; 28, 465):



Isodiphenyldihydrotetrazine Diphenyldihydrotetrazine Diphenyltetrazine.

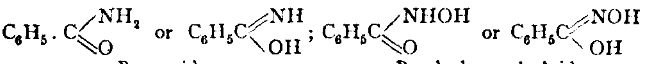
19. **Formazyl Derivatives** of the Aromatic Monocarboxylic Acids (compare p. 129). *Formazyl-benzene*, $C_6H_5C\left\langle\begin{matrix}N=N.C_6H_5\\N—NH.C_6H_5\end{matrix}\right.$, melting at 173°, consists of red leaflets with greenish metallic reflex. It is produced (1) when diazobenzene (p. 129) in alkaline solution (B. 27, 1690) acts upon benzaldehyde-phenyl hydrazone; (2) from benzenyl amidoxime (p. 208) and phenylhydrazine (B. 27, 160); (3) when phenylhydrazine and benzphenylhydrazid imide chloride (p. 203) interact. The hetero-ring formations of the formazyl compounds have been described (p. 130). A glacial acetic acid solution of sulphuric acid converts formazyl benzene into *phenphenyltriazine* (see this). It yields *triphenyltetrazolium hydroxide* upon oxidation:



Phenphenyltriazine
Triphenyltetrazolium Hydroxide.

Guanazyl Benzene, $C_6H_5C\left\langle\begin{matrix}N.NHC(NH_2):NH\\N:NC_6H_5\end{matrix}\right.$, orange-yellow prisms, melting at 199°. It is formed when diazobenzene chloride acts upon benzalamido guanidine, the condensation product derived from benzaldehyde and amidoguanidine (1, 415). Nitric acid oxidizes guanazyl benzene to *diphenyl tetrazole* (B. 30, 444).

20. **Hydroxamic Acids, their Ethers and Esters.**—Under benzamide mention was made of the two structural formulas which were theoretically possible for benzamide: the *benzamid*-formula and the *benzimido*-acid formula. If we suppose in these formulas an hydrogen atom in union with nitrogen to be replaced by the hydroxyl group, we arrive at the two formulas theoretically possible for an hydroxamic acid:



Benzamide Benzhydroxamic Acid.

The amid-formula is preferred for the amides of the carboxylic acids; the imido-ethers are derived from the imido-acid formula. The oximido-acid formula is, however,

more probable for the benzhydroxamic acids. *Hydroxime-acid chlorides* correspond to the imide-chlorides, and *amidoximes* to the amidines.

Numerous ethers and esters can be obtained from an hydroxamic acid. This is accomplished by replacing one or both hydrogen atoms of the $C\genfrac{}{}{0pt}{}{\diagup NOH}{\diagdown OH}$-group by alkyl- or acidyl-groups. Although hydroxamic acid and its homologues are known in but one form each, many ethereal derivatives of the hydroxamic acids occur in several similarly constituted modifications, whose demonstrated difference can in no satisfactory way be attributed to structural difference (W. Lossen, A. **281**, 169). Just as in the case of the oximes, so here the isomeric phenomena of benzhydroxamic acid ethers are referred to the stereochemistry of nitrogen.

α- and β-Ethylbenzhydroxamic acids differ from each other by the following space-formulas (Werner, B. **25**, 33):

$$\begin{array}{l} C_6H_5C{-}O\,.\,C_2H_5 \\ \quad\ \ | \\ HO\,.\,N \end{array} \quad \text{Ethylsynbenzhydroxamic Acid } (\alpha\text{-}) \qquad \begin{array}{l} C_6H_5\,.\,C{-}O\,.\,C_2H_5 \\ \qquad\ | \\ \quad\ N\,.\,OH \end{array} \quad \text{Ethylantibenzhydroxamic Acid } (\beta\text{-}).$$

Crystallographic studies have shown that many classes of amide-like derivatives of hydroxylamine appear in polymorphous modifications.

Benzhydroxamic Acid, $C_6H_5\,.\,C(:NOH)\,.\,OH$, melting at 124°, and *Dibenzhydroxamic Acid* or *Benzoylbenzhydroxamic Ester*, $C_6H_5C(:NO\,.\,COC_6H_5)OH$, melting at 161°, are produced by the interaction of benzoyl chloride and hydroxylamine. The potassium salt of the dibenzhydroxamic acid is decomposed by water, especially on heating, into potassium benzoate, s-*diphenylurea*, and CO_2:

$$2C_6H_5C(:NOCOC_6H_5)\,.\,OK + H_2O = 2C_6H_5COOK + CO(NHC_6H_5)_2 + CO_2.$$

The rearrangement occurring here recalls that of the ketoximes (Beckmann, p. 189) to alkylized acid amides. As s-diphenylurea can be resolved by hydrochloric acid into aniline and CO_2, it is possible, aided by these reactions, capable of greater generalization, to change benzoic acid to aniline—that is, to replace the CO_2H-group by the NH_2-group (A. **175**, 313; compare benzoyl azide, p. 201). The alkyl ethers of dihydroxamic acid are known in two modifications: α-(syn.)-*Methyl Ether*, melting at 53°; β-(anti)-*Methyl Ether*, melting at 55°; α-(syn.)-*Ethyl Ether*, melting at 58°; β-(anti)-*Ethyl Ether*, melting at 63° (A. **205**, 281; **281**, 235). The α-bodies result from the action of alkyl iodides upon the silver salts; the β-compounds through the action of benzoyl chloride and caustic potash upon the alkylhydroximic acids.

Benzhydroximic Acid Alkyl Ethers or **Alkyl Benzhydroximic Acids,** C_6H_5-$C(:NOH)OR'$, are obtained from benzimido-ethers and hydroxylamine hydrochloride, and from dibenzhydroxamic acid alkyl ethers (A. **252**, 211). They occur in two modifications, which can be distinguished by the fact that the α- or syn.-modifications yield in treatment with PCl_5 (by Beckmann's transposition) phenylcarbamic acid ethers or their transposition products:

$$\begin{array}{c} C_6H_5COCH_3 \\ \| \\ HON \end{array} \longrightarrow \begin{array}{c} OCOCH_3 \\ | \\ C_6H_5\,.\,NH \end{array};$$

whereas the β- or anti-forms become phosphoric ethers of the alkylbenzhydroximic acids (B. **29**, 1146). α-(syn.)-*Methyl Ether*, melting at 64°, readily changes to a physical isomeride; this is also true of the syn.-modification, melting at 101° (B. **29**, 1150). β-(anti)-*Methyl Ether* melts at 44°, α-(syn.)-*Ethyl Ether* melts at 53°, and β-(anti)-*Ethyl Ether* at 68°.

The alkylbenzhydroximic acids also form alkyl and acidyl ethers. **Tribenzoyl Hydroxylamine,** $C_6H_5\,.\,C(:NOCOC_6H_5)O\,.\,COC_6H_5$, is produced in three forms when benzoyl chloride acts upon hydroxylamine hydrochloride: α-modification, melting at 100°; β-modification, melting at 141°; and the γ-modification, melting at 112°. Hydrochloric acid changes the α- and γ-modifications to the β-form (A. **281**, 276).

21. Haloids of Benzhydroximic Acid.—The free chlorides, as well as the ethers of the fluorides, chlorides, and bromides, are known. The free chlorides result from the

corresponding benzaldoximes upon treatment with chlorine in chloroform solution. The ethers are produced when the amidoxime ethers are treated with haloid acids and an alkaline nitrite; also when PCl_5 acts upon the alkyl ethers of hydroxamic acid (A. **252**, 217).

Benzhydroximic Acid Chloride, $C_6H_5C(:NOH)Cl$, melting at 48°, from benzaldoxime, is converted by ammonia into benzenylamidoxime (B. **27**, 2193, 2846). *Benzenyl-methoxime Chloride*, $C_6H_5.C(:NOCH_3)Cl$, boils at 225°. *Benzenyl-methoxime Bromide*, $C_6H_5.C(:NOC_2H_5)Br$, boils at 239° (B. **24**, 3454).

Benzenylhydroxylamine-acetic Acid, $C_6H_5.C(:NOCH_2.CO_2H).OH$, melting at 135° to 138°, is formed when caustic potash acts upon *benzenylnitroxime-acetic acid*, $C_6H_5.C(:NO.CH_2CO_2H)ONO$, melting at 95°. The latter is produced through the action of sulphuric acid and potassium nitrite upon benzenylamidoxime-acetic acid (see below). *Benzenylfluor-*, *chlor-*, and *bromoxime-acetic Acids* all melt at 135°. They are obtained when haloid acids and an alkaline nitrite are allowed to act upon benzenylamidoxime-acetic acid (B. **26**, 1570).

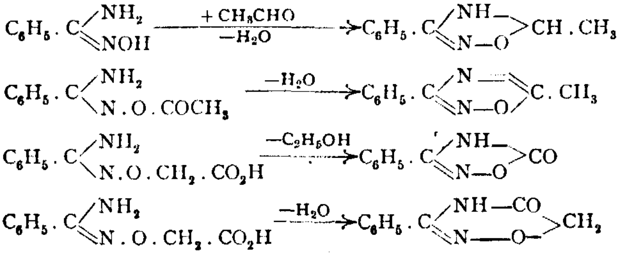
22. The **Amidoximes** are produced by the action of hydroxylamine upon thioamides, nitriles, imido-ethers (p. 203), and amidines (p. 204). Ferric chloride imparts a deep red color to the alcoholic solution of the amidoximes.

Benzenylamidoxime, Amide of Benzhydroxamic Acid, $C_6H_5.C\begin{matrix}\diagup N(OH)\\ \diagdown NH_2\end{matrix}$, melts at 79°. It gives the isonitrile reaction with chloroform and potassium hydroxide. Nitrous acid changes it to benzamide. With acids and caustic alkalies it yields salts—*e. g.*, $C_6H_5.C(:N.OH)NH_2.HCl$ and $C_6H_5.C(NH_2):N.OK$. Alkyl iodides convert the latter into amidoxime-ethers.

Methyl Ether, $C_6H_5(.NH_2):NOCH_3$, melts at 57°; the *ethyl ether* melts at 67° (A. **281**, 280).

Acetylbenzenylamidoxime, $C_6H_5.C(:NOCOCH_3).NH_2$, melts at 16° (B. **18**, 1082). *Benzenyloximidocarbonic Ester*, $C_6H_4C(.NH_2):NOCO_2C_2H_5$, melts at 127°. *Benzenyl-oximidoglycollic acid*, $C_6H_5.C(.NH_2):NO.CH_2.CO_2H$, melts at 123°. *Benzenyl-amidoxime-butyric acid*, $C_6H_5C(NH_2):NOCH(C_2H_5)COOH$, melts at 82° (B. **29**, 2655).

Hetero-ring Formations of the Amidoximes.—(1) The amidoximes condense with the aldehydes of the fatty series to *hydrazoximes*. The amidoxime acid derivatives, alluded to above, throw off, on heating above their melting points, water or alcohol, and become *azoximes*:



Benzenylhydrazoxime Ethidene

Ethenyl-benzenyl Azoxime

Carbonyl-benzenyl Azoxime

Anhydride of benzenylamidoxime Glycollic Acid.

23. **Aromatic Nitrolic Acids**, like $C_6H_5.C(:N.OH)NO_2$, are not yet known (B. **27**, 2193).

Derivatives of Orthobenzoic Acid (compare I. 233).

24. **Ethyl Orthobenzoic Ester**, *Ethyl Orthobenzoate*, *Benzenylethyl Ether*, C_6H_5-$C(O.C_2H_5)_3$, from phenyl chloroform and sodium ethylate, boils at 220–225°.

25. **Benzotrichloride**, *Phenylchloroform*, *Benzoic Acid Trichloride*, *Benzenyl Trichloride*, $C_6H_5CCl_3$, melting at −22.5° (B. **26**, 1053), boiling at 213°, with sp. gravity 1.38 (14°), is isomeric with the chlorbenzalchlorides, dichlorbenzylchlorides, and the trichlortoluenes. Phenyl chloroform bears the same relation to benzoic acid or phenyl formic acid that methyl chloroform sustains to acetic acid or methyl formic acid (I, 256).

It results (1) upon conducting chlorine into boiling toluene, until there is no further increase in weight (A. 146, 330); (2) by the action of phosphorus pentachloride upon benzoyl chloride (A. 139, 326). It changes to benzoic acid when heated to 100° with water. It yields benzoyl chloride and benzoic anhydride on being digested with anhydrous oxalic acid. It readily condenses to triphenyl methane derivatives with the anilines and phenols (B. 15, 232; A. 217, 223).

26. **Orthobenzoic Acid Piperidide,** $C_6H_5C(N.C_5H_{10})_3$, melting at 80°, is produced on warming benzotrichloride and piperidine.

The *benzamide haloids* also belong to the derivatives of orthobenzoic acid (p. 203).

SUBSTITUTED AROMATIC MONOCARBOXYLIC ACIDS.

Only those will be given in connection with the monocarboxylic acids in which the substitution has occurred with the hydrogen atoms of the benzene nucleus. Certain ortho-products show the power, by water elimination, of yielding inner anhydrides or heterocyclic compounds.

See p. 197 for the behavior of 2,6-substituted carboxylic acids in their esterification with alcohol and hydrochloric acid.

1. **Halogen Benzoic Acids** are formed:

(1) By the substitution of benzoic acids or nitriles; the halogen atom entering first prefers the meta-position with reference to carboxyl (p. 69).

(2) By oxidizing p- and m-halogen toluenes and higher homologues with chromic acid, and o-haloid hydrocarbons with dilute nitric acid or potassium permanganate.

(3) From the amido-acids (*a*) by means of the diazo-sulphates, or (*b*) the diazoamido-acids; both classes when boiled with haloid acids yield haloid carboxylic acids. Thus, the fluor-benzoic acids have been obtained from the diazoamidobenzoic acids (B. 15, 1197).

(4) By the action of phosphorus pentachloride upon the oxy-acids (compare salicylic acid).

(5) Nucleus synthesis: heating the halogen nitrobenzenes to 200–230° with potassium cyanide and alcohol. In this reaction the cyanogen-group replaces the nitro-group; it does not, however, take the same position in the benzene residue (B. 8, 1418). At the temperature of the reaction the nitrile changes to the acid. m-Chlornitrobenzene yields o-chlorbenzoic acid; and p-chlornitrobenzene, m-chlorbenzoic acid.

(6) From the haloid anilines through the diazo-compounds, etc.

Properties and Deportment.—In the following tabulation of the melting points of the mono-haloid benzoic acids it will be observed that the ortho-bodies melt at the lowest temperatures and the para-compounds at the highest. The melting point rises with the atomic mass of the substituting halogen. The ortho-derivatives are rather readily soluble in water, and yield easily soluble barium salts, whereby they can usually be quite readily separated from the meta- and para-derivatives. When they are fused with caustic potash oxy-benzoic acids result.

Fluorbenzoic Acid:	o-: melts at 118°;	m-: melts at 124°;	p-: melts at 181°.
Chlorbenzoic Acid:	o-: " " 137°;	m-: " " 153°;	p-: " " 240°.
Brombenzoic Acid:	o-: " " 147°;	m-: " " 155°;	p-: " " 251°.
Iodbenzoic Acid:	o-: " " 162°;	m-: " " 187°;	p-: " " 265°.

Numerous polychlor- and polybrom-benzoic acids are known. The five hydrogen atoms of the phenyl of benzoic acid can be replaced by chlorine or bromine.

2. **Iodoso- and Iodo-benzoic Acids** (p. 60).—Upon chlorinating the three

iodbenzoic acids in chloroform three iodide-chloridebenzoic acids are produced. Sodium hydroxide changes these to the iodoso-benzoic acids (B. **27**, 2326). o-*Iodosobenzoic Acid*, $C_6H_4(IO)CO_2H$, consists of brilliant leaflets, which explode at 244°. This acid is also produced in the oxidation of o-iodbenzoic acid with fuming nitric acid (B. **28**, 83), and together with o-*iodobenzoic acid*, $C_6H_4(IO_2)CO_2H$, exploding at 230° with violence, when o-iodbenzoic acid is oxidized with potassium permanganate. The formula $C_6H_4\left\{\begin{matrix}[1]I(OH) \\ [2]CO\text{ —}\end{matrix}\right\rangle O$ has also been suggested for the o-iodosobenzoic acid, as it yields, like lævulinic acid, when heated with acetic anhydride, an acetyl derivative: *acetiodosobenzoic acid*, $C_6H_4\left\{\begin{matrix}[1]I(OCOCH_3) \\ [2]CO\text{ ———}\end{matrix}\right\rangle O$, melting at 166° (B. **26**, 1364).

3. Nitromonocarboxylic Acids.

3. **Nitromonocarboxylic Acids.**—Not more than three nitro-groups have been introduced into the benzene residue of an aromatic carboxylic acid.

Nitrobenzoic Acids.—(1) Metanitrobenzoic acid is the principal product in the nitration of benzoic acid. The quantity of the ortho (20 per cent.) and para (1.8 per cent.) acids is less (A. **193**, 202). (2) By oxidizing the three nitrotoluenes; the ortho with potassium permanganate (B. **12**, 443), and the meta and para with a chromic acid mixture (A. **155**, 25). o- and p-Nitrobenzoic acids are also produced by oxidizing o- and p-nitrobenzyl chloride with potassium permanganate (B. **17**, 385), as well as by oxidizing o- and p-nitrocinnamic acids. (3) By converting the three isomeric nitranilines into the three nitrobenzonitriles (B. **28**, 150; constitution, pp. 38, 105). The nitration of o-benzonitrile yields m-nitrobenzonitrile almost exclusively. o-Nitrobenzonitrile has been obtained from o-nitraniline (B. **28**, 151). Nitro-acids result upon saponifying the nitronitriles with caustic soda:

o-*Nitrobenzoic Acid* melts at 147°;	o-*Nitrobenzonitrile* melts at 109°.
m-*Nitrobenzoic Acid* " " 141°;	m-*Nitrobenzonitrile* " " 116°.
p-*Nitrobenzoic Acid* " " 238°;	p-*Nitrobenzonitrile* " " 147°.

o-Nitrobenzoic Acid possesses a sweet taste and dissolves in 164 parts of water at 16°. Its nitration produces 2,6-, 2,5-, 2,4-dinitrobenzoic acids, and styphnic acid (p. 161). m-Nitrobenzoic acid dissolves in 425 parts of water (16°). Its barium salt dissolves with difficulty. Upon nitration it yields 2,5-dinitrobenzoic acid. p-Nitrobenzoic acid, called also *nitrodracrylic acid*, because it is formed in the action of nitric acid upon dragon's blood (p. 193) (A. **48**, 344), is very sparingly soluble in water. Nitration converts it into 2,4- and 3,4-dinitrobenzoic acids. The electrolysis of its warm sulphuric acid solution produces p-amidophenolsulphonic acid (B. **28**, R. 378; compare also B. **28**, R. 126). 2,4-, 3,4-Dinitro- and 2,4,6-trinitrobenzoic acids are obtained by the oxidation of the corresponding nitroluenes (p. 68). The dinitrotoluenes are oxidized by a chromic acid mixture (B. **27**, 2209), or by potassium permanganate. Trinitrotoluene is oxidized by a nitric-sulphuric acid mixture at 150–200°.

2,4-*Dinitrobenzoic Acid* melts at 179°; the 2,5-acid melts at 177°; 2,6-acid at 202°; the 3,4-acid at 165°; the 3,5-, or *ordinary* dinitrobenzoic acid melts at 204°. 2,4,6-*Trinitrobenzoic Acid*, $(NO_2)_3C_6H_2CO_2H$, melts at 210° with the elimination of CO_2 (B. **27**, 3154; **28**, 2564, 3065; R. 125).

Nitro-haloid Benzoic Acids.—o,o-*Fluornitrobenzoic Acid*, $C_6H_3F(NO_2)COOH$, melting at 127°, has been prepared by oxidizing fluornitrotoluene. In contrast with the other o,o-disubstituted benzoic acids it can be quite readily esterified (see p. 197; B. **29**, 842). The nitration of m-brombenzoic acid yields two o-nitro-acids, both of which yield anthranilic acid upon reduction: 3-brom-2-nitrobenzoic acid, melting at 250°, and 3-brom-6-nitrobenzoic acid, melting at 139° (compare equivalence of the six hydrogen atoms of benzene, p. 33). The halogen atom in the nitrohaloid benzoic acids is reactive, like that in the nitrohaloid benzenes (B. **22**, 3282).

Nitrophenyl-acetic Acids, $NO_2 . C_6H_4 . CH_2 . CO_2H$, are produced by saponifying the nitrobenzylcyanides with caustic alkali. The latter bodies constitute the product resulting from the action of potassium cyanide upon the nitrobenzyl chlorides (p. 180),

(B. **16**, 2064; **19**, 2635). The nitration of phenyl-acetic acid produces mainly the p-nitro-body, with little of the o-nitro-acid and o,p-dinitrophenyl acetic acid, melting at 166°.

o-, m-, p-Nitrophenylacetic Acids melt at 141°, 120°, 152°.
o-, m-, p-Nitrobenzyl Cyanides " " 84°, 61°, 116°.

Nitrohydrocinnamic Acids, $NO_2C_6H_4CH_2 . CH_2 . CO_2H$.—p-Nitro- and o-nitro-hydrocinnamic acids result from the nitration of hydrocinnamic acid. Both in turn yield the o,p-dinitro-acid. The o-nitro-acid is also prepared from o-nitro-p-amidohydrocinnamic acid, the first reduction-product of the o,p-dinitro-acid, as well as from o-nitrobenzyl-malonic ester (see this). The m-nitro-acid is obtained from p-acetamido-m-nitrohydro-cinnamic acid (B. **15**, 846; **29**, 635; compare also m-nitrotoluene, p. 68).

o-, m-, p-Nitrohydrocinnamic Acids melt at 115°, 118°, 163°.
o-p-Dinitrohydrocinnamic Acid melts at 123° (B. **13**, 1680).

o- and p-**Nitrohydratropic Acids**, $NO_2 . C_6H_4 . CH(CH_3) . CO_2H$, melting at 110° and 87°, are produced upon introducing hydratropic acid into strongly cooled, fuming nitric acid (A. **227**, 262).

4. **Nitrosomonocarboxylic Acids**.—o-*Nitrosobenzoic Acid*, $C_6H_4[1]NO[2]CO . OH$, melting with decomposition at 210°, results from the oxidation of the phenyl-oxyindols obtained from benzoïnoxime (B. **29**, 2064).

4. AROMATIC AMIDOMONOCARBOXYLIC ACIDS.

These are obtained by reducing the corresponding nitrobenzoic acids. Like glycocoll, the amidobenzoic acids yield crystalline salts both with acids and bases. They do not combine with acetic acid, hence are precipitated by it from their alkali salts.

Like glycocoll, these acids can be considered as cyclic ammonium salts (1, 354). The hydrogen atoms of the amido-group are replaceable by alkyl and acidyl residues. Dimethylated amido-acids are produced by the action of phosgene and aluminium chloride upon the dimethyl-anilines. Acetamidobenzoic acids are formed by the oxidation of the acetyl toluidines.

The o-amido-acids (of which o-amidobenzoic acid and o-amido-phenylacetic acid are closely related to indigo, and o-amidohydrocin-namic acid to quinoline) form hetero-rings, and yield rather remarkable ortho-condensation products.

Anthranilic Acid, o-*Amidobenzoic Acid*, $C_6H_4\begin{cases}[1]CO_2H\\ [2]NH_2\end{cases}$, or $C_6H_4\begin{cases}[1]COO\\ \quad\diagup\\ [2]NH_3\end{cases}$, melts at 145°, and breaks down, upon heating, into aniline and carbonic acid. Its aqueous solution has a sweet taste. It was first obtained from *indigo* (see this) by the action of caustic potash (Fritzsche, 1841). The oxidation can be accelerated by the addition of manganese dioxide (A. **234**, 146). The acid results from the reduction of o-nitro-benzoic acid and the two m-brom-o-nitrobenzoic acids (p. 210) with tin and hydrochloric acid; also from phthalimide upon treatment with bromine and caustic potash (B. **24**, R. 966), as well as from anthranil, acet-anthranilic acid, and isatoic acid (see below).

Nitrous acid converts anthranilic acid in aqueous solution into sali-

cylic acid, and sodium in amyl alcohol solution into hexahydroanthranilic acid, hexahydrobenzoic acid (see this), and n-pimelic acid (1, 444) (B. 27, 2466).

The *ethyl ether* boils at 260°. It is formed when alcohol and hydrochloric acid act upon isatoic acid. Its *amide*, from isatoic acid and ammonia, melts at 108° (B. 18, R. 273). *Phenylanthranilic acid*, $C_6H_5NH[2]C_6H_4[1]CO_2H$, melts at 181° (B. 25, 1734) (below).

Formylanthranilic acid, $CHO.NH[2]C_6H_4[1]CO_2H$, melting at 168°, is produced in boiling isatoic acid with formic acid.

Acetylanthranilic Acid, $CH_3CO.NH[2]C_6H_4[1]CO_2H$, results when o-acetyltoluidine is oxidized, when o-amidobenzoic acid and anthranil are acted upon with acetic anhydride, and in the oxidation of methyl ketol and quinaldine with potassium permanganate. It melts at 185°. The *ethyl ester*, melting at 61°, and the *amide*, melting at 170°, are produced from the corresponding anthranilic acid derivatives by the action of acetic anhydride.

Benzoylanthranilic Acid melts at 183° (B. 26, 1304).

Anthranil, o-Amidobenzoic Acid Lactam, $C_6H_4\begin{cases}[1]CO \\ [2]NH\end{cases}$ or $C_6H_4\begin{cases}[1]CH \\ [1]N\end{cases}\!\!>O$, is an oil which volatilizes readily with aqueous vapor, possesses a peculiar odor, and boils with decomposition at about 210°. This inner anhydride of o-amidobenzoic acid has never been obtained from the acid itself, but (1) by the reduction of o-nitrobenzaldehyde with ferrous sulphate (theoretical quantity) and ammonia (B. 15, 2105, 2572), or with tin and glacial acetic acid (B. 16, 2227; 28, 1382). It also results (2) when o-nitrophenyloxyacrylic acid is boiled with water (B. 16, 2222); anthroxanaldehyde is produced at the same time. It dissolves in alkalies, forming salts of anthranilic acid. o-Amidobenzaldehyde and o-amidobenzylalcohol are produced when it is reduced.

Methylcarboxyanthranilic Ester, $CO_2H.NH[2]C_6H_4[1]CO_2CH_3$, melting at 176°, is formed, together with anthranilic ester, when methyl alcohol at 130° acts upon isatoic acid (B. 20, R. 813).

Carboxyethylanthranilamide, $CO_2C_2H_5.NH[2]C_6H_4[1]CONH_2$, melting at 152°, results when $ClCO_2C_2H_5$ acts upon anthranilamide.

o-*Uramidobenzoic Acid*, $NH_2CONH[2]C_6H_4[1]CO_2H$, melting at 152°, is formed in the interaction of the chlorhydrate of anthranilic acid and potassium cyanate.

Isatoic Acid, *Anthranilcarbonic Acid*, $C_6H_4\begin{cases}[1]CO \\ [2]N.CO_2H\end{cases}$ or $C_6H_4\begin{cases}CO.O \\ NH.CO\end{cases}$(?), melts about 233–240°, decomposing at the same time into carbon dioxide and anthranil. It was first obtained by oxidizing a glacial acetic acid solution of indigo with chromic acid (H. Kolbe, 1885), and later from anthranil and anthranilic acid by the action of chlorcarbonic esters (B. 22, 1672). It is very sparingly soluble in water. Digested with alkalies or boiled with acids, it decomposes into carbon dioxide and anthranilic acid. Ammonia, hydrazine, phenylhydrazine, and hydroxylamine change it into the corresponding amide derivatives of anthranilic acid (B. 19, R. 65; 26, R. 585).

Kynuric Acid, *Oxalylanthranilic Acid*, *Carbostyrilic Acid*, $CO_2H.CONH[2]C_6H_4[1]CO_2H + H_2O$, becomes anhydrous at 100° and melts at 180° with decomposition. It is formed from the quinoline derivatives—kynurine (see this), kynurenic acid (see this), α-phenylquinoline (see this), carbostyril (see this), acettetrahydroquinoline, and indoxylic acid (see this)—by oxidation. It is prepared synthetically by heating anthranilic acid with oxalic acid to 130° (B. 17, 401; R. 110). Its *ethyl ester*, $CO_2.C_2H_5.CO.NH[2]C_6H_4[1]CO_2H$, is formed in the oxidation of the ester of indoxylic acid (B. 15, 778). It melts at 180°.

Dicyanaminobenzoyl, $C_6H_4\begin{cases}[1]CO.N \\ [2]NH.C.CN\end{cases}$, melts with decomposition. It results from cyanogen and o-amidobenzoic acid in aqueous solution (B. 11, 1986). *Ethoxycyanaminobenzoyl*, $C_6H_4\begin{cases}[1]CO.N \\ [2]NH.C.OC_2H_5\end{cases}$, melting at 173°, is formed from cyanogen

and o-amidobenzoic acid in alcoholic solution (B. 2, 415). Ammonia changes it to o-benzglycocyamidine, *benzoylenguanidine*, $C_6H_4\begin{cases}[1]CO.NH \\ [2]NH.\overset{|}{C}:NH\end{cases}$, which CH_3I in strong alkaline solution converts into α-o-benzcreatinine, $C_6H_4\begin{cases}[1]CO\text{———}NH \\ [2]N(CH_3)\text{—}\overset{|}{C}:NH\end{cases}$ (B. 13, 977). Further derivatives of anthranilic acid have been obtained from o-amidobenzonitrile, $C_6H_4[1]NH_2[2]CN$, melting at 47°; this results in the reduction of o-nitronitrile (B. 29, 624).

Dibromanthranilic Acid is produced when bromine acts upon o-nitrotoluene (p. 68).

Hetero-ring Formations of Anthranilic Acid and its Derivatives.—Anthranil and isatoic acid, whose constitution has not yet been definitely determined, are derivatives of anthranilic acid which certainly contain an hetero-ring, but both are not formed from anthranilic acid. However, numerous reactions of the latter acid lead to hetero-rings, which contain one, two, and three nitrogen atoms in the new ring (compare o-amidobenzylalcohol, p. 180; o-amidobenzylamine, p. 181; o-amidobenzaldehyde, p. 187, and o-amidoacetophenone, p. 190).

Acetylanthranilic acid and phenol condense on heating to *acridone*, which also results on digesting phenylanthranilic acid (p. 212) with concentrated sulphuric acid (B. 25, 2740). Anthranilic acid condenses with acetophenone and acetoacetic ester to *quinoline* derivatives (B. 27, 1396):

$$C_6H_4\begin{cases}[1]CO_2H \\ [2]NHC_6H_5\end{cases}\xrightarrow{\quad -H_2O \quad}C_6H_4<\begin{matrix}CO \\ NH\end{matrix}>C_6H_4$$ Acridone

$$C_6H_4\begin{cases}[1]COOH \\ [2]NH_2\end{cases}+\begin{matrix}CH_2.CO_2.C_2H_5 \\ | \\ CO.CH_3\end{matrix}\xrightarrow[-HO_2]{-C_2H_6O}C_6H_4<\begin{matrix}C(OH)=C.CO_2H \\ | \\ N===C.CH_3\end{matrix}$$ γ-Oxyquinaldine-β-carboxylic Acid

$$C_6H_4\begin{cases}[1]COOH \\ [2]NH_2\end{cases}+\begin{matrix}CH_3 \\ | \\ CO.C_6H_5\end{matrix}\xrightarrow{\quad -2H_2O \quad}C_6H_4<\begin{matrix}C(OH)=CH \\ | \\ N===C.C_6H_5\end{matrix}$$ α-Phenyl-γ-oxyquinoline.

o-*Benzoylenurea* is formed on heating anthranilic acid and anthranilamide with urea. It also results upon heating carboxethyl-o-amidobenzamide (B. 2, 416; 22, R. 196), as well as by the action of mineral acids upon uramidobenzoic acid (B. 27, 976). *Ketodihydroquinazolines* are produced on heating formyl-, acetyl-, and benzoyl-o-amidobenzamide. The β-methyl compound is formed in the action of acetamide upon anthranilic acid, and ammonia upon ethylacetamidobenzoic ester (B. 20, R. 630; 22, R. 196; 27, R. 516). The condensation products of o-amidobenzoic acid and cyanogen gas have been described and formulated (p. 212):

$$\left.\begin{matrix}C_6H_4\begin{cases}[1]COOH \\ [2]NH.CO.NH_2\end{cases}\xrightarrow{-H_2O} \\ C_6H_4\begin{cases}[1]CONH_2 \\ [2]NH.COOC_2H_5\end{cases}\xrightarrow{-C_2H_6O}\end{matrix}\right\}\longrightarrow C_6H_4\begin{cases}CO—NH \\ NH—\overset{|}{C}O\end{cases}$$ o-Benzoylenurea Diketotetrahydroquinazoline (see this)

$$C_6H_4\begin{cases}[1]CO.NH_2 \\ [2]NH.CHO\end{cases}\xrightarrow{\quad -H_2O \quad}C_6H_4<\begin{matrix}CO.NH \\ | \\ N=CH\end{matrix}$$ δ-Keto-dihydroquinazoline.

Nitrous acid converts anthranilamide directly into benzazimide, whereas the o-diazobenzoic ester first resulting from anthranilic ester must be treated with ammonia to effect this change (B. 21, 1538; R. 571):

$$\left.\begin{matrix}C_6H_4\begin{cases}[1]CONH_2 \\ [2]NH_2.HCl\end{cases}\xrightarrow{\qquad NOOH \qquad} \\ C_6H_4\begin{cases}[1]CO.OC_2H_5 \\ [2]NH_2.HCl\end{cases}\xrightarrow{NOOH}C_6H_4\begin{cases}COOC_2H_5 \\ N=N.Cl\end{cases}\xrightarrow{NH_3}\end{matrix}\right]\longrightarrow C_6H_4<\begin{matrix}CO—NH \\ | \\ N=N\end{matrix}$$ Benzazimide.

m- and p-*Amidobenzoic Acids* melt at 173° and at 186°.

Chrysanisic Acid, 3,5-Dinitro-4-amidobenzoic acid, $(NO_2)_2(NH_2) . C_6H_2CO_2H$, melting at 259°, consists of golden yellow leaflets, and is produced when 3,5-dinitro-4-methoxybenzoic acid is heated with aqueous ammonia.

Diamidobenzoic Acids, $(NH_2)_2C_6H_3CO_2H$, are prepared by reducing the dinitro- and the nitroamidobenzoic acids. They break down in dry distillation into carbon dioxide and phenylenediamines (p. 94). Like the o-phenylenediamines (p. 95), the diamidobenzoic acids, containing two amido-groups in the ortho-position with reference to each other, readily yield hetero-cyclic derivatives—*e. g.*, nitrous acid converts 3,4-diamidobenzoic acid into 3,4-*azimidobenzoic acid* (B. 15, 1880) (p. 96). The m,p- and the p,m-amidouramidobenzoic acids yield two different uramidoazimidobenzoic acids, which afford the same azimidobenzoic acid by saponification (B. 29, R. 586).

3,4,5-*Triamidobenzoic Acid*, $(NH_2)_3 . C_6H_2 . CO_2H$, from chrysanisic acid by reduction, breaks down, when heated, into CO_2 and 1,2,3-triamidobenzene (A. 163, 12). 2,3,5-*Triamidobenzoic Acid* (B. 15, 2199).

Many amido-acids, derived from alkyl-benzoic acids, are known; also haloid amido-acids, nitro-amido-acids, etc.

Amidophenyl-fatty Acids are obtained from the nitrophenyl-fatty acids. Certain o-amidophenyl-fatty acids are particularly noteworthy because of their tendency to form inner anhydrides: γ- or δ-*lactams* (I, 359), which is so great that the corresponding free o-amido-acids are not capable of existing—*e. g.*, o-amidophenyl-acetic acid and o-amidophenylhydrocinnamic acid.

m- and p-*Amidophenyl-acetic Acids* melt at 149° and 200°.
m- and p-*Amidohydrocinnamic Acids* " " 84° " 131°.

4-*Amido*-3-*nitrohydrocinnamic Acid*, from p-acetamidohydrocinnamic acid, melts at 145°.

p-*Amidohydratropic Acid*, melting at 128°, is converted into phloretic acid (A. 227 267) by nitrous acid.

γ- and δ-Lactams of the o-Amidophenyl-fatty Acids.—Anthranil can be regarded as the simplest o-amido-acid lactam. However, its constitution has not been satisfactorily established, and it has not been obtained from anthranilic acid. The next higher homologues are:

Oxindol, the lactam of o-*Amidophenyl-acetic Acid*, $C_6H_4\left\{\begin{matrix}[1]\,CH_2 . CO\\ [2]\,NH\text{——}|\end{matrix}\right.$, melting at 120°, is obtained by the reduction of o-nitrophenyl-acetic acid with tin and hydrochloric acid, and from dioxindol with sodium amalgam. If heated to 150° with baryta-water it is converted into the barium salt of o-amidophenyl-acetic acid, from which oxindol is separated by acids (B. 16, 1704). Nitrous acid converts it into isatoxime (see this).

Oxindol boiled with acetic anhydride yields *Aceto-oxindol*, $C_6H_4\left\{\begin{matrix}[1]\,CH_2.CO\\ [2]\,N <^{}_{CO.CH_3}\end{matrix}\right.$, melting at 126°. It dissolves to *aceto-o-amidophenyl-acetic acid*, $CH_3 . CO . NH . C_6H_4 . CH_2 . CO_2H$, melting at 142°. Heated with alkalies or acids it breaks down into oxindol and acetic acid.

p-*Amido-oxindol*, $NH_2 . C_8H_6NO$, melting about 200°, is formed by the reduction of 2,4-dinitrophenyl-acetic acid (p. 211) with tin and hydrochloric acid. If ammonium sulphide be used as the reducing agent, the product will be 4-*Amido-2-nitrophenyl-acetic acid*, melting at 185° (B. 14, 824); compare o-nitrophenylisonitroso-acetic acid.

Atroxindol, lactam of o-amidohydratropic acid, $C_6H_4\left\{\begin{matrix}[1]\,CH(CH_3) . CO\\ [2]\,NH\text{————}|\end{matrix}\right.$, melts at 119°.

Hydrocarbostyril, *lactam of Amidohydrocinnamic Acid*, melting at 163°, is formed by the reduction of o-nitrohydrocinnamic acid with tin and hydrochloric acid (Glaser and Buchanan, 1869) (B. 15, 2103), and by heating hydrocarbostyril-carboxylic acid, result-

ing from the reduction of o-nitrobenzylmalonic acid (B. **29**, 667). Hydrocarbostyril sustains the same relation to quinoline that oxindol bears to indol:

$$C_6H_4\begin{cases}[1]CH_2.CH_2\\ [2]NH\ .\ \overset{|}{C}O\end{cases}, \text{ Hydrocarbostyril};\quad C_6H_4\begin{cases}[1]CH = CH\\ [2]N = \overset{|}{C}H\end{cases}, \text{ Quinoline.}$$

p-*Amidohydrocarbostyril*, $NH_2C_9H_8NO$, melting at 211°, is formed, together with 4-amido-2-nitrohydrocinnamic acid, melting at 139°, from 2,4-dinitrohydrocinnamic acid.

5. **Diazobenzoic Acids** (p. 98) are produced from the mineral acid salts of the amidobenzoic acids with nitrous acid, just as the ordinary diazo-bodies are obtained from the aniline salts. Nitrous acid converts the amide of o-amidobenzoic acid into *benzazimide* (p. 213). *Nitrates* of the three diazobenzoic acids are produced from the nitrates of the three amidobenzoic acids. They explode violently on the application of heat. The *perbromides* of the three diazobenzoic acids are also known. When the nitrates are boiled with water they yield oxybenzoic acids; the *sulphates* are converted by haloid acids into haloid benzoic acids (B. **18**, 960). The free diazobenzoic acids are very unstable. The *diazide* of *anthranilic acid*, $C_6H_4\begin{cases}[1]CO\\ [2]N_2\end{cases}\!\!>O$, consists of white, glistening needles. It is obtained when the chloride is acted upon with silver oxide (B. **29**, 1535).

6. **Diazoamidobenzoic Acids** (p. 106) are formed when nitrous acid is conducted into the alcoholic solution of the amidobenzoic acids. *Diazo*-m-*amidobenzoic Acid*, $CO_2H[1]C_6H_4[3]N = N - NH[3']C_6H_4[1']CO_2H$, is an orange-red powder. Hydrofluoric acid converts it into m-fluorbenzoic acid (p. 114):

$$\begin{matrix}CO_2H[1]C_6H_4[3]N= \\ CO_2H[1]C_6H_4[3]NH\end{matrix}\!\!>N + 2HFl = \begin{matrix}CO_2H[1]C_6H_4[3]Fl \\ CO_2H[1]C_6H_4[3]NN_2HFl\end{matrix} + N_2.$$

7. **Diazoïmidobenzoic Acids**, $\begin{matrix}N\\ \|\\ N\end{matrix}\!\!>N\ .\ C_6H_4CO_2H$ (p. 110), result upon letting ammonia act upon the perbromides of diazobenzoic acids, or when hydrazine-benzoic acids are treated with nitrous acid. The o-body melts about 70°; the *meta* at 160°, and the p-compound at 185° (B. **9**, 1658).

8. **Azoxybenzoic Acids**, $O\!\!<\!\begin{matrix}N\ .\ C_6H_4CO_2H\\ |\\ N\ .\ C_6H_4CO_2H\end{matrix}$, are formed in the reduction of the nitrobenzoic acids with alcoholic potash (p. 111). The o-derivative is also produced when n-oxyindolcarboxylic acid (see this) is oxidized with alkaline potassium permanganate (B. **17**, 1904; **24**, R. 666; **29**, 656).

9. **Azobenzoic Acids**, $\begin{matrix}N\ .\ C_6H_4\ .\ CO_2H\\ |\\ N\ .\ C_6H_4\ .\ CO_2H\end{matrix}$. The action of sodium amalgam upon the mononitrobenzoic acids produces these acids.

Azobenzene-p-*monocarboxylic acid* has been obtained from amidoazobenzene (B. **19**, 3022). o-, m-, and p-Azobenzoic acids are decomposed on fusion. *Azophenylene* or *phenazine* is formed when the calcium salts are distilled.

10. **Hydrazine-benzoic Acids.**—The symmetrical hydrazobenzoic acids result when the azobenzoic acids are reduced with sodium amalgam, or with ferrous sulphate and sodium hydroxide. o-*Hydrazobenzoic Acid* melts at 205°. m-*Hydrazobenzoic Acid*, $CO_2H[3]C_6H_4[1]\cdot NH\ .\ NH[1']C_6H_4[3']CO_2H$. These two acids, when boiled with hydrochloric acid, rearrange themselves to diamidodiphenyldicarboxylic acids (see these). The rearrangement of the m-acid into p-diamidodiphenic acid is of importance for the proof of the constitution of diphenic acid (see this), and consequently that of phenanthrene.

o-, m-, and p-*Hydrazine-benzoic Acids*, $NH_2.NH\ .\ C_6H_4.CO_2H$, re-

sult when the hydrochlorides or nitrates of diazobenzoic acids are reduced. Thionyl aniline converts them into o-, m-, and p-*benzoic-acid thionyl hydrazones*, melting at 155°, 231°, and 258° (B. **27**, 2555).

o-Hydrazine-benzoic acid, when heated, changes to a *lactam of o-hydrazine-benzoic acid*, $C_6H_4\left\{\begin{matrix}[1]CO\\ [2]NH\end{matrix}\right\rangle NH$, melting at 242° with decomposition (A. **212**, 333).

11. **Sulphobenzoic Acids.**—On conducting the vapors of SO_3 into benzoic acid, we obtain as chief product m-*Sulphobenzoic Acid*, and in smaller amount p-*Sulphobenzoic Acid* (A. 178, 279).

The three isomerides can be obtained by oxidizing the three toluene sulphonic acids with an alkaline solution of potassium permanganate (p. 192).

If the toluene sulphamides, instead of the free acids, be subjected to similar oxidation, the m- and p-toluene sulphamides yield m- and p-sulphamine-benzoic acids; whereas the o-toluene sulphamide changes to benzoic sulphinide, or anhydrosulphamine-benzoic acid, called *saccharin* (B. **12**, 469). Hydrochloric acid reconverts this at 150° into o-sulphobenzoic acid.

o-*Sulphobenzoic Acid* when anhydrous melts at 250°. In deportment it recalls phthalic acid (see this). It forms, for example, phthaleïns, an anhydride and an imide. PCl_5 produces two dichlorides, melting at 22° and 76°, which probably have the formulas $C_6H_4\left\{\begin{matrix}COCl\\ SO_2Cl\end{matrix}\right.$ and $C_6H_4\left\{\begin{matrix}CCl_2\\ SO_2\end{matrix}\right\rangle O$ (B. **29**, R. 355). o-*Sulphobenzoic Anhydride*, $C_6H_4\left\{\begin{matrix}[1]CO\\ [2]SO_2\end{matrix}\right\rangle O$, melting at 118°, is obtained from the acid by the action of acetyl chloride. The *nitrile*, o-*cyanbenzene-sulphonic acid*, $C_6H_4(CN)SO_3H$, is obtained from the o-aniline sulphonic acid (p. 137) through the diazo-compound (B. **28**, R. 751).

o-*Sulphamine-benzoic Acid*, $SO_2NH_2[2]C_6H_4[1]CO_2H$, melts at 153–155°, changing at the same time into the sulphinide. It is produced by oxidizing o-toluene sulphamide with potassium ferricyanide (B. **19**, R. 689), and from its inner anhydride by digesting with caustic soda. Isomeric o-*Benzamide-sulphonic acid*, $C_6H_4(CONH_2)SO_3H$ (B. **29**, R. 102), is formed when sulphobenzoic acid is fused with ammonium sulphocyanide (B. **29**, R. 102).

o-Anhydrosulphamine-benzoic Acid, *Benzoic Sulphinide*, $C_6H_4\left\{\begin{matrix}[1]CO\\ [2]SO_2\end{matrix}\right\rangle NH$, called **saccharin**, melts at 220°. It was discovered in 1879 by Ira Remsen and C. Fahlberg. Its preparation was given above. This compound is now made technically in very large quantities. It is used for sweetening purposes. It is 500 times sweeter than cane-sugar. It dissolves with difficulty in cold water, and, like succinimide and phthalimide, behaves like a strong acid, forming imide-salts. The sodium salt, $C_6H_4\left\{\begin{matrix}[1]CO\\ [2]SO_2\end{matrix}\right\rangle NNa$, is very readily soluble in water, and is 400 times sweeter than cane-sugar. It is readily transposed by such haloid derivatives as benzyl chloride and acetyl chloride to N-derivatives of saccharin (B. **25**, 1737; **29**, 1048).

o-*Sulphobenzoic-anil*, $C_6H_4\left\{\begin{matrix}SO_2\\ CO\end{matrix}\right\rangle N.C_6H_5$, melting at 190°, results from the action of aniline upon the chlorides of sulphobenzoic acid (B. **29**, R. 353). Phosphorus pentachloride converts saccharin into *pseudosaccharin-chloride*, $C_6H_4\left\{\begin{matrix}[1]CCl\\ [2]SO_2\end{matrix}\right\rangle N$, melting at 149° (B. **29**, 2995).

All sulpho-acids containing the sulpho-group in the o-position with reference to the carboxyl group of an alkylbenzoic acid are capable of forming *sulphinides* or *sulphocarbonimides* (B. **25**, 1737).

3,5-*Disulphobenzoic Acid* is produced by sulphonating benzoic acid with H_2SO_4 and P_2O_5 (B. **27**, R. 118). 2,4-*Disulphobenzoic Acid* is obtained from 2,4-toluene-disulphonic acid (B. **14**, 1205).

(1 *b*). MONOHYDRIC OXYPHENYL-PARAFFIN ALCOHOLS AND THEIR OXIDATION PRODUCTS.

1. MONOHYDRIC OXYPHENYL-PARAFFIN ALCOHOLS, OR PHENOL ALCOHOLS.

These alcohols contain, in addition to the alcoholic hydroxyl, other hydroxyl groups joined to the benzene nucleus, which impart to them the character of phenols. Some of the alcohols of this group are simple transposition products of long-known plant substances.

Formation.—Some of the methods described under the benzyl alcohols also lead to phenol alcohols:

(1) The reduction of corresponding aldehydes and ketones.

(2) The treatment of aldehydes with caustic alkali.

(3) The action of sodium amalgam upon amides (B. **24**, 175).

(4) They are linked to the benzyl alcohols through the amidophenyl-paraffin alcohols, which nitrous acid converts into oxyphenyl-paraffin alcohols.

(5) *Nucleus-synthesis:* Methylene chlorides (B. **13**, 435) or formaldehyde and sodium hydroxide (B. **27**, 2411; J. pr. Ch. [2] **50**, 225) change phenols into phenyl alcohols.

Monoxybenzyl Alcohols, $HOC_6H_4 . CH_2OH$.—The three theoretically possible isomerides have been prepared. They result when the corresponding aldehydes are reduced with sodium amalgam. *Saligenin,* or o-Oxybenzyl alcohol, is the best-known member of the group:

o-Oxybenzyl Alcohol melts at 82°.
m-Oxybenzyl " " 67°.
p-Oxybenzyl " " 110°.

Saligenin, or o-*Oxybenzyl Alcohol,* was first obtained in the decomposition of the glucoside *salicin* (see this) by means of emulsin, ptyaline, or dilute acids (Piria, 1845; A. **56**, 37):

$$\underset{\text{Salicin}}{C_6H_{11}O_5 . O . C_6H_4 . CH_2 . OH} + H_2O = HO . C_6H_4 . CH_2 . OH + \underset{\text{Glucose.}}{C_6H_{12}O_6}$$

Saligenin has also been prepared by the common methods from salicylaldehyde, salicylamide, o-amidobenzyl alcohol, and phenol. It is soluble in hot water, alcohol, and ether. Ferric chloride produces a deep blue color in its solutions. Acids resinify it, forming *saliretin* (*ῥητίνη*, resin). Ethers and substitution products of saligenin are known. These have been made in part from the corresponding salicyl-derivatives.

o-*Oxybenzylamine,* Salicylamine, melts at 121° (B. **23**, 2744).

p-*Oxyphenylethylamine,* see tyrosine (see this).

Anisyl Alcohol, p-Methoxybenzyl Alcohol, $CH_3O[4]C_6H_4[1] . CH_2 . OH$, is obtained from anisic aldehyde by alcoholic potassium hydroxide. It melts at 45° and boils at 259°. It forms anisic aldehyde when oxidized.

p-*Homosaligenin,* $CH_3[5]C_6H_3[2](OH)CH_2 . OH$, melts at 105°.

Hydrocumarone, $C_6H_4\left\{\begin{matrix}[1]CH_2 . CH_2\\ [2]O\text{———}|\end{matrix}\right.$, boiling at 188°, is the inner anhydride of o-oxyphenyl-ethyl alcohol, not known in the free state. It is formed when sodium in alco-

hol acts upon cumarone (B. **25**, 2409). p-*Thymotin Alcohol*, $CH_3[2]C_3H_7[5]C_6H_2[4]$-$OH[1]CH_2 . OH$, melts at 120° (B. **27**, 2412).

Dioxybenzyl Alcohols are not known in a free condition, but derivatives of 2,5-dioxy- and of 3,4-dioxybenzyl alcohol have been obtained in the reduction of certain aldehyde-ethers with sodium amalgam. *Dimethyl-gentisin Alcohol*, $(CH_3O)_2[2,5]C_6$-$H_3[1]CH_2 . OH$, boils at 278°.

Vanillyl Alcohol, $CH_3O[3]HO[4]C_6H_3[1]CH_2 . OH$, from vanillin, melts at 115°.

Piperonyl Alcohol, $CH_2<\begin{matrix}O[3]\\O[4]\end{matrix}\}C_6H_3[1]CH_2 . OH$, from piperonal, melts at 51°.

o-*Dioxybenzylamine* melts at 168° (B. **27**, 1799).

2. AROMATIC OXYMON-ALDEHYDES, PHENOL ALDEHYDES.

The phenol aldehydes are obtained (1) by oxidizing the phenol alcohols with chromic acid; (2) by an important nucleus-synthetic method, consisting in letting chloroform and an alkaline hydroxide act upon phenols (reaction of Reimer) when the chloroform enters the o- and p-position with reference to the phenol hydroxyl, and is then converted into the aldehyde group (B. **9**, 1268):

$$C_6H_5 . OH + CHCl_3 + 4KOH = C_6H_4<\begin{matrix}OK\\CHO\end{matrix} + 3KCl + 3H_2O.$$

Behavior.—All the phenol aldehydes show the same reactions of the aldehyde group as the benzaldehydes. Oxidizing agents convert them with difficulty into oxyacids; this is most easily accomplished by fusion with caustic alkalies. They reduce an ammoniacal silver solution, but not the Fehling solution. They dissolve in alkalies, forming salts—*e. g.*, $C_6H_4(CHO) . ONa$; the alkyl iodides convert the latter into alkyl ethers.

a. **Monoxybenzaldehydes**, $HO . C_6H_4 . CHO$.—Three are possible according to theory; all of them are known. Anisic aldehyde, the methyl ether of p-oxybenzaldehyde, has been known for the longest period.

Salicylic Aldehyde, o-*Oxybenzaldehyde*, formerly called *salicylous* or *spiroylous* acid, boils at 196°. Its sp. gravity equals 1.172 (15°). It occurs in the volatile oils of the different varieties of *Spiræa*—*e. g.*, *Spiræa ulmaria*. It is obtained by the oxidation of saligenin and salicin (Piria, 1839) and by the decomposition of *helicin*, an oxidation product of salicin (see this). It is most readily prepared (together with p-oxybenzaldehyde) by the action of chloroform and caustic potash upon phenol. It is separated from the p-body by distillation in steam, in which salicylic aldehyde is very volatile. It is rather easily soluble in water; the solution is colored a deep violet by ferric chloride (compare saligenin, p. 217, and salicylic acid, p. 222). Like all ortho-oxyaldehydes, it colors the skin an intense yellow. Sodium amalgam transforms it into saligenin; oxidizing agents change it to salicylic acid.

Potassium salicylic aldehyde, $C_6H_4(OK)CHO + H_2O$, consists of yellow plates. The *methyl ether*, $C_6H_4(O . CH_3) . CHO$, melts at 35° and boils at 238°; the *ethyl ether* boils at 248°. The *acet-derivative*, $CH_3 . CO . O . C_6H_4 . CHO$, melts at 37° and boils at 253°. *Glucose-derivative*, see *Helicin*. o-*Aldehydophenoxy-acetic acid*, $CO_2H . CH_2O$-$[2]C_6H_4[1]CHO$, melting at 132°, splits off water and becomes coumarilic acid (see this). *Salicyl aldoxime* melts at 57°; comp. B. **22**, 3320. o-*Anisaldoxime*, $CH_3O . [2]C_6H_4$-

[1]CH : N(OH), melts at 92° (B. **23**, 2741). The *phenylhydrazone* melts at 142° (B. **18**, 1660).

Consult B. **22**, 2339, upon the nitrosalicylaldehydes.

m-**Oxybenzaldehyde** results in the reduction of m-oxybenzoic acid with sodium amalgam (B. **14**, 969) and from m-nitrobenzaldehyde (B. **15**, 2045). It melts at 104° and boils at 240°. Its *oxime* melts at 87°. Its *hydrazone* melts at 130° (B. **24**, 826). Its nitration produces three mononitro-compounds. See B. **18**, 2572, for the nitro-m-methoxybenzaldehydes.

p-**Oxybenzaldehyde** is formed from phenol, chloroform, and caustic alkali, together with salicylic aldehyde. It melts at 116°, and sublimes. Its *aldoxime* melts at 65°; its *hydrazone* at 178°. Consult B. **29**, 2302, 2355, for the haloid p-oxybenzaldehydes. Its methyl ether, readily accessible, is the so-called—

Anisic Aldehyde, p-Methoxybenzaldehyde, $CH_3O[4]C_6H_4[1]$-CHO, boiling at 248°, with sp. gr. 1.123 (15°). It results in oxidizing anethol (see this), present in various essential oils (anise, fennel, etc.), with dilute nitric acid or a chromic acid mixture.

Homologous Monoxybenzaldehydes have been prepared from various phenols by Reimer's method (p. 218). Thus:

			M.P.	B.P.	
o-Cresol	. . . gave	o-Homosalicylic Aldehyde,	17°	208°	(B. **24**, 3667).
		o-Homo-p-oxybenzaldehyde,	115°		
m-Cresol	. . . "	m-Homosalicylic Aldehyde,	54°	222°.	
		m-Homo-p-oxybenzaldehyde,	110°		
p-Cresol	. . . "	p-Homosalicylic Aldehyde,	56°	217°.	
Pseudocumenol	"	[3,5,6]-Trimethyl Salicylic Aldehyde,	105°		(B. **18**, 2656).
Thymol . . .	"	p-Thymotin Aldehyde,	133°		(B. **16**, 2097).
Carvacrol, . .	"	p-Carvacrotin Aldehyde,	liquid		(B. **19**, 14).
p-Isobutylphenol	"	p-Isobutyl Salicylic Aldehyde,	"	252°	(B. **28**, R. 468).

The o-oxybenzaldehydes are more readily soluble in water and more sparingly soluble in chloroform than the p-oxybenzaldehydes. The o-bodies are volatile in steam, form sparingly soluble sodium bisulphite derivatives, and are colored yellow by ammonia (B. **11**, 770); compare coumarines.

b. **Dioxybenzaldehydes.**—Some of the dioxybenzaldehydes which have been prepared by the chloroform-potash reaction are ethereal derivatives of protocatechuic aldehyde, and are characterized by an agreeable odor. This is especially true of *vanillin* and *piperonal*, or *heliotropine*. Both substances are prepared on a technical scale:

$$C_6H_3\begin{cases}[1]CHO\\ [3]OH\\ [4]OH\end{cases} \qquad C_6H_3\begin{cases}[1]CHO\\ [3]OCH_3\\ [4]OH\end{cases} \qquad C_6H_3\begin{cases}[1]CHO\\ [3]O\\ [4]O\end{cases}\!>CH_2$$

Protocatechuic Aldehyde — Vanillin — Piperonal.

Protocatechuic Aldehyde, 3,4-*Dioxybenzaldehyde*, melting at 153° (B. **26**, R. 701), was first obtained from piperonal (Fittig and Remsen, 1871); also from vanillin, iso-vanillin, and opianic acid with dilute hydrochloric acid. It is prepared in the nucleus-synthetic way from pyrocatechin by the chloroform reaction. It dissolves readily in water. Ferric chloride colors its aqueous solution a deep *green* (p. 159). It reduces ammoniacal silver solutions. Molten caustic potash converts protocatechuic aldehyde into protocatechuic acid. Its *phenylhydrazone* exists in two modifications: α- (stable), melting at 176°, and β- (unstable), melting at 121–128°. Its *oxime* melts at 150° (B. **29**, R. 670).

Vanillin, m-*Methoxy*-p-*oxybenzaldehyde*, melting at 80°, sublimes readily, and is the active constituent of the vanilla bean pod (*Vanilla*

planifola), which contains about two per cent. (B. **9**, 1287) of it. Vanillin also occurs in the orchid *Nigritella suaveolens* (B. **27**, 3049). It was first prepared artificially from the glucoside coniferine (see this) by its oxidation with chromic acid (Tiemann and Haarmann, 1874; B. **7**, 613). Glycovanillin (see this) was obtained as an intermediate product in the oxidation of coniferine; acids or emulsin split it up into glucoses and vanillin (B. **18**, 1595, 1657). Vanillin is also produced by oxidizing eugenol (see this) (B. **9**, 273). In the nucleus-synthetic way it has also been formed, together with m-methoxyl-salicylic aldehyde, boiling at 266°, from guaiacol, chloroform, and caustic potash (B. **14**, 2023).

Heated with HCl it decomposes into CH_3Cl and protocatechuic aldehyde. It behaves like a p-oxybenzaldehyde, and protocatechuic acid results on fusion with potassium hydroxide—two facts from which its constitution may be concluded. Nascent hydrogen converts vanillin into vanillyl alcohol, hydrovanilloïn, corresponding to hydrobenzoïn.

Vanillin-oxime melts at 117° (B. **24**, 3654).

Trithiovanillin, $[C_6H_3(OH)(OCH_3)CSH]_3$, melts at 236° (B. **29**, 143).

Isovanillin, p-*Methoxy*-m-*oxybenzaldehyde*, melting at 116°, smells, when heated, like vanilla and anise oil. It is obtained by oxidizing hesperitinic acid or by heating opianic acid with hydrochloric acid.

Dimethylprotocatechuic Aldehyde, $C_6H_3(O.CH_3)_2CHO$, melts at about 42° and boils near 283° (B. **11**, 662).

Piperonal, *Protocatechuic Aldehyde-methylene Ether*, *Heliotropine*, $(CH_2O_2)C_6H_3$-CHO, melting at 37° and boiling at 263°, was obtained by the oxidation of piperic acid (see this). It is also formed by treating protocatechuic aldehyde with alkali and methylene iodide. Its odor is pleasant, like that of heliotrope. Piperonylic acid results from its oxidation and piperonyl alcohol from its reduction (p. 218). Its *oxime* melts at 110°. Its *phenylhydrazone* melts at 100°. PCl_5 converts it into *piperonal chloride*, (CH_2O_2)-$C_6H_3CHCl_2$, and *dichlorpiperonal chloride*, $(CCl_2O_2).C_6H_3CHCl_2$, which is changed by cold water into *dichlorpiperonal*, $(CCl_2O_2).C_6H_3CHO$, and with warm water it yields CO_2, HCl and protocatechuic aldehyde (A. **159**, 144; B. **26**, R. 701). *Brompiperonal*, $(CH_2O_2).C_6H_2Br.CHO$ (B. **24**, 2592). o-*Nitro-piperonal* yields bidioxymethylene indigo (B. **24**, 617). The following bodies have been prepared from resorcinol and hydroquinone by the action of chloroform and caustic alkali, just as protocatechuic aldehyde was made from pyrocatechin.

β-Resorcylaldehyde, $(HO)_2[2,4]C_6H_3[1]CHO$, melts at 135°.
Gentisin-aldehyde, $(HO)_2[2,5]C_6H_3[1]CHO$, melts at 99°.

Dioxyaldehydes are also produced in dilute solutions when much chloroform and caustic potash are used. The monomethyl ethers of resorcinol and hydroquinone, like guaiacol, each yield, upon treatment with chloroform and potash, two aldehydes—one, comparable in deportment with salicylaldehyde, contains the aldehyde group in the o-position with reference to phenol hydroxyl; while the other contains the aldehyde group in the p-position, referred to the free phenol hydroxyl (B. **14**, 2024).

c. **Tri- and Tetraoxybenzaldehydes.**—Alkyl ethers of these bodies have been formed by oxidizing aromatic plant derivatives, containing unsaturated aliphatic side-chains (B. **16**, 2112; **17**, 1086; **24**, 3818).

Glycosyringaldehyde, an oxidation product of *syringine* (see this), when treated with emulsin yields a trioxybenzaldehyde ether (B. **22**, R. 107).

3. PHENOL KETONES.

They have been obtained (1) from amidoketones (B. **18**, 2691) and (2) from aromatic *β*-ketone-carboxylic acids (B. **25**, 1308). The nucleus-synthetic methods, consisting in the introduction of acid radicals into phenols and phenol ethers, are better adapted for

the purpose; (3) the condensation of phenols with glacial acetic acid and other fatty acids by zinc chloride or tin tetrachloride (B. **14**, 1566; **23**, R. 43; **24**, R. 770); better still, by phosphorus oxychloride (B. **27**, 1983); (4) from phenols by means of acid chlorides (B. **22**, R. 746); (5) from phenol alkyl ethers and acid chlorides in the presence of aluminium chloride (B. **23**, 1199).

o-*Oxyacetophenone*, boiling at 213°, is formed by method 2. p-*Oxyacetophenone*, melting at 107°, is produced by method 1. p-*Acetylanisol*, p-methoxyacetophenone, melting at 38° and boiling at 258°, is formed by method 3. *Propionylphenol*, HOC_6H_4-COC_2H_5, melting at 148°, is produced by method 4.

Acetopyrocatechol, $(HO)_2[3,4]C_6H_3[1]CO.CH_3$, melts at 116° (B. **27**, 1989). *Acetvanillon*, $HO[4](CH_3O)[3]C_6H_3[1]COCH_3$, melting at 115°, is produced in the oxidation of aceteugenol, and synthetically from guaiacol by method 5 (B. **24**, 2855, 2869). *Acetoveratron*, $(CH_3O)_2C_6H_3.CO.CH_3$, melts at 48° (B. **27**, 1989). *Acetopiperone*, $(CH_2O_2)[3,4]C_6H_3[1]CO.CH_3$, melting at 87°, results on oxidizing protocotoïn with potassium permanganate (B. **24**, 2989; **25**, 1127; **26**, 2348).

Resacetophenone, $(HO)_2[2,4]C_6H_3[1]CO.CH_3$, melting at 142°, is produced by method 3, and from β-methylumbelliferone upon fusion with caustic potash (B. **16**, 2123). Its p-methyl ether—

Pæonol, $CH_3O[4](HO)[2]C_6H_3.CO.CH_3$, melting at 45°, occurs in the root-bark of *Pæonia Moutan*, a ranunculus from Japan (B. **25**, 1292). When resorcinol diethyl ether is acetylated with the aid of aluminium chloride the products are 1,2,4 *Resacetophenone Diethyl Ether*, melting at 69°, and an *isomeric* resacetophenone with the melting point 178° (B. **29**, R. 386). Consult B. **29**, R. 674, for haloid resacetophenones.

Quina-acetophenone, $(HO)_2[2,5]C_6H_3[1]CO.CH_3$, melting at 202°, is produced by method 2. *Valerohydroquinone*, $(HO)_2[2,5]C_6H_3.CO.C_4H_9$, melts at 115°. Its quinhydrone results when sunlight acts upon benzoquinone and valeric aldehyde (B. **24**, 1344).

Gall-acetophenone $(HO)_3[2,3,4]C_6H_2[1]CO.CH_3$, melting at 168°, is formed by method 3 (B. **27**, 2737).

4. PHENOL MONOCARBOXYLIC ACIDS.

The aromatic oxy-acids containing hydroxyl united to the benzene nucleus combine the character of acids and phenols, hence are designated *phenol acids*. Should the hydroxyl groups enter the aliphatic side-chains, we would obtain aromatic alcohol acids, showing in their deportment very great similarity to the oxy-fatty acids.

Formation.—A. *From substituted carboxylic acids, as in the case of the phenols:* (1) Through the conversion of the amido-acids, by means of nitrous acid, into diazo-compounds and then boiling the latter with water. (2) By fusing the sulphobenzoic acids with alkalies. The haloid benzene carboxylic acids react like the sulpho-acids when subjected to similar treatment.

B. From compounds in which the phenol hydroxyl is always present. (3) By fusing homologous phenols with alkalies, when the methyl group, linked to the nucleus, will be oxidized to the carboxyl group. (4) By oxidizing the sulphuric or phosphoric acid esters of homologous phenols and then saponifying the resulting phenol-carboxylic esters. (5) By fusing the phenol aldehydes, difficult to oxidize, with alkalies. (6) By converting the phenol aldoximes into oxy-acid nitriles and then saponifying the latter.

Nucleus-synthesis: (7) By the action of carbon dioxide upon the dry sodium salts of the phenols at elevated temperatures, when the carbonic acid generally enters the ortho-position with reference to the hydroxyl

group. This reaction will be more exhaustively discussed in connection with salicylic acid.

(8) By boiling the phenols with carbon tetrachloride (1, 387) and caustic potash (B. **10**, 2185):

$$C_6H_5.OH + CCl_4 + 5KOH = C_6H_4\begin{matrix}\diagup OH \\ \diagdown CO_2K\end{matrix} + 4KCl + 3H_2O.$$

This reaction is perfectly analogous to that of the formation of oxyaldehydes by means of chloroform and caustic alkali. As a general thing the carboxyl group enters the para-position with reference to phenol hydroxyl. o-Oxy-acids are produced in smaller amounts.

(9) When urea chloride, phenylisocyanate, and phenyl mustard oil, together with aluminium chloride, act upon phenol ethers (or thiophenol ethers) in carbon disulphide solution (A. **244**, 61; B. **27**, 1733), the products are amides, anilides, and thioanilides of alkyl oxy-acids.

Behavior.—They are monobasic acids. The hydrogen of the carboxyl group is alone replaced by metals when they are acted upon with alkaline carbonates.

Their hydroxyl hydrogen can also be replaced by alkalies, forming *basic* salts—*e.g.*, $C_6H_4\begin{matrix}\diagup ONa \\ \diagdown CO_2Na\end{matrix}$. Carbon dioxide, however, will convert the latter into *neutral* salts. The ether esters manifest a like deportment, inasmuch as it is only the alkyl ester which is eliminated, with the production of a salt of an alkyl-ether acid:

$$C_6H_4\begin{matrix}\diagup O.CH_3 \\ \diagdown CO_2.CH_3\end{matrix} + KOH = C_6H_4\begin{matrix}\diagup O.CH_3 \\ \diagdown CO_2K\end{matrix} + CH_3.OH.$$

The o-oxy-acids, unlike the m- and p-derivatives, volatilize in aqueous vapor, are colored violet by ferric chloride, and dissolve in chloroform. The m-oxy-acids are colored reddish-brown when heated with concentrated sulphuric acid, with the formation of oxyanthraquinones (B. **18**, 2142). They are usually more stable than the o- and p-acids. Boiling concentrated hydrochloric acid decomposes the p-acids into carbon dioxide and phenols. All the oxy-acids decompose into carbon dioxide and phenols when distilled with lime.

A. *Monoxy-mono-carboxylic Acids.*—Salicylic acid or o-oxybenzoic acid is by far the most important representative of this class. It is extensively applied both in therapeutics and in the color industry.

Monoxybenzoic Acids.—The three isomerides theoretically possible are known.

Salicylic Acid, o-Oxybenzoic Acid, $HO[2]C_6H_4[1]CO_2H$, melting at 155°, occurs in a free condition in the buds of *Spiræa ulmaria*, as the methyl ester in oil of *Gaultheria procumbens* (oil of wintergreen), a species of Ericaceæ. It is produced, by the general methods of formation, (1) from anthranilic acid; (2) from o-sulpho-, o-chlor-, and o-brombenzoic acids; (3) from o-cresol; (4) from saligenin and salicylaldehyde; (5) from phenolates with CO_2; and (6) with carbon tetrachloride.

It is also formed upon fusing *coumarin* (see this) and *indigo* (see this) with caustic potash, and in the distillation of copper benzoate.

Technical Preparation.—Two methods of bringing sodium phenolate and CO_2 in reaction are applicable for this purpose:

(*a*) Sodium phenoxide is heated in a current of carbon dioxide at 180–220°, when the

latter is absorbed. Half of the phenol distils over, and the residue consists of disodium salicylate (H. Kolbe):

$$2C_6H_5.ONa + CO_2 = C_6H_4\begin{cases}ONa \\ CO_2Na\end{cases} + C_6H_5.OH.$$

The behavior of potassium phenolate in this reaction is remarkable. At 150° dipotassium salicylate is produced. At a more elevated temperature, however, there is formed with the dipotassium salicylate its isomeride, dipotassium paraoxybenzoate. The latter is more abundant in proportion to the increased temperature, until at 220° it is the sole product. The primary alkali salicylates, when heated, show the following deportment:

Monosodium salicylate at 220° yields disodium salicylate, phenol, and CO_2:

$$2C_6H_4\begin{cases}CO_2Na \\ OH\end{cases} = C_6H_4\begin{cases}CO_2Na \\ ONa\end{cases} + C_6H_5OH + CO_2.$$

Primary potassium salicylate at 220° yields phenol, dipotassium paraoxybenzoate, and CO_2.

Primary sodium paraoxybenzoate at 280° yields phenol, CO_2, and disodium salicylate (J. pr. Ch. [2] **16**, 425).

(*b*) Sodium phenoxide is saturated under pressure, in closed vessels, with carbon dioxide, when it is converted into sodium phenocarbonate, $C_6H_5.O.CO_2Na$. By continuing the pressure and applying a heat of 120–130°, this salt is changed to sodium salicylate: $HO[2]C_6H_4[1]CO_2Na$. The second method shows a complete transformation of the phenol.

History.—Piria first obtained salicylic acid in 1838, when he oxidized its aldehyde with molten caustic potash (A. **30**, 165). In 1843 Cahours proved that wintergreen oil consisted almost entirely of methyl salicylic ester (A. **53**, 332). Gerland in 1853 showed that anthranilic acid, as suspected by A. W. Hofmann, could be converted by nitrous acid into salicylic acid (A. **86**, 147). In 1860 H. Kolbe and Lautemann prepared it synthetically from phenol, sodium, and carbonic acid (A. **115**, 201). It was Kolbe who first correctly interpreted salicylic acid to be a monobasic oxyacid, and in 1874 discovered that the acid could readily be formed upon conducting carbon dioxide over dry and heated sodium phenate. It was in this way that he ascertained the conditions serving for the production of the acid upon a technical scale. R. Schmidt discovered the conversion of sodium phenocarbonate under pressure at 120–130° into monosodium salicylate (B. **17**, R. 624).

Properties and Behavior.—Salicylic acid crystallizes from alcohol in colorless prisms; from hot water in long needles. It has a sweet, acid taste. It dissolves in 400 parts of water at 15°, and in 12 parts at 100°; it is very soluble in chloroform. When it is heated alone, *salol*, or phenylsalicylic ester, and *xanthone* (see this) are produced (A. **269**, 323). Sodium in amyl alcohol solution reduces it to normal pimelic acid. In this reaction the ring is ruptured and ketohexamethylene carboxylic acid appears as an intermediate product (B. **27**, 331).

Its aqueous solution acquires a violet coloration upon the addition of ferric chloride. It is a powerful antiseptic, arrests decay and fermentation (Kolbe, J. pr. Ch. [2] **10**, 9), and is applied therapeutically both as the free acid and in the form of its sodium salt (in rheumatism of the joints).

Salicylates.—*Sodium Salicylate*, $HO.C_6H_4CO_2Na$, is a crystalline powder with an unpleasant sweet taste. *Basic Calcium Salicylate*, $(OC_6H_4CO_2)Ca + H_2O$, dissolves with great difficulty, and is precipitated upon boiling salicylic acid with lime-water. It serves for the separation of salicylic acid from m- and p-oxybenzoic acids.

Esters, Ethers, and Ether Esters.—*Methyl Ester*, $HO.C_6H_4.CO_2.CH_3$, boiling at 224°, with sp. gr. 1.197 (0°), is the chief ingredient of wintergreen oil (from *Gaultheria procumbens*). It occurs in many different plants in the form of a glucoside (B. 29, R. 511).

When the methyl ester is digested with an alcoholic solution of potassium hydroxide and methyl iodide, we get the *dimethyl ester*, $C_6H_4.\langle^{OCH_3}_{CO_2.CH_3}$, boiling at 245°. Boiled with potassium hydroxide it is saponified, yielding methyl alcohol and methyl salicylic acid, $C_6H_4\langle^{O.CH_3}_{CO_2H}$, melting at 98°. It decomposes into carbon dioxide and anisol when heated to 200°.

Phenol Salicylic Ester, *Salol*, $HO.C_6H_4.CO_2.C_6H_5$, melting at 43° and boiling at 172° (12 mm.), results on heating salicylic acid alone to 200–220°, with the elimination of water and carbon dioxide; from salicylic acid, phenol, and $POCl_3$; from polysalicylide on heating with phenol, or when phosgene acts upon the sodium salts of salicylic acid and phenol. It is applied as an antiseptic. It changes to *xanthone* (see this), or diphenylene ketone oxide, when it is heated. When *sodium salol*, $C_6H_4(ONa).CO_2.C_6H_5$ (from salol and sodium), is heated to 280–300°, it changes to the isomeric sodium salt of *phenylsalicylic acid*, $C_6H_4(O.C_6H_5).CO_2H$, which melts at 113°, and is not colored by ferric chloride.

Thiosalol, $HO.C_6H_4COSC_6H_5$, melting at 54°, results upon heating salicylic acid and thiophenol with PCl_3 or $POCl_3$. *Phenylthiosalicylic Acid*, $C_6H_5SC_6H_4CO_2H$, melts at 166° (A. 263, 2). See Thioxanthone.

Aceto-salicylic Acid, $CH_3CO.O.C_6H_4.CO_2H$, melts at 118°.

Salicyl Chloride, $HO.C_6H_4COCl$, is not known. It is true that PCl_5 acts very energetically upon salicylic acid, but the resulting phosphoroxychloride is transposed by the phenol hydroxyl, with evolution of hydrochloric acid:

$$C_6H_4\begin{cases}[1]COOH\\ [2]OH\end{cases} \xrightarrow{PCl_5} C_6H_4\begin{cases}[1]COCl\\ [2]OH\end{cases} \xrightarrow{POCl_3} C_6H_4\begin{cases}[1]COCl\\ [2]OPOCl_2\end{cases},$$

and there results:

o-*Chlorcarbonylphenyl-orthophosphoric acid dichloride*, melting at 168° (11 mm.). If the PCl_5 continues to act, this compound will exchange an oxygen atom for two chlorine atoms, and o-*Trichlormethylphenyl-orthophosphoric acid dichloride*, $(Cl_2PO)O[2]C_6H_4[1]CCl_3$, boiling at 178° (11 mm.) will be formed. When this is heated with PCl_5 in a sealed tube to 180°, there results:

o-*Chlorbenzotrichloride*, $Cl[2]C_6H_4[1]CCl_3$, melting at 30° and boiling at 130° (11 mm.) (A. 239, 314). m- and p-Oxybenzoic acids, as well as m- and p-cresotinic acids, behave similarly.

If, however, the hydrogen atom of the phenol hydroxyl is replaced by the methyl or acetyl group, then PCl_5 produces the chlorides:

Methyl Salicyl Chloride, $CH_3O[2]C_6H_4[1]COCl$, boiling at 254°, and *Acetyl Salicyl Chloride*, $CH_3CO_2[2]C_6H_4[1]COCl$, melting at 43° and boiling at 135° (12 mm.).

When halogen atoms, nitro groups, or methyl groups are introduced into salicylic acid, and then occupy the o-position with reference to the phenol hydroxyl, the latter will be protected by them from the attack of the phosphorus oxychloride. Consequently, in the action of PCl_5 *free oxychlorides* will be produced:

o-*Cresotinic Chloride*, $HO[2]C_6H_3[3]CH_3[1]COCl$, melting at 28°; 3-*Chlorsalicyl Chloride*, melting at 63°; [3,5]-*Dichlorsalicyl Chloride*, melting at 79°, and [3,5]-*Dichlornitrosalicyl Chloride*, melting at 70° (B. 30, 221).

The influence of substituents in the vicinity of the phenol hydroxyl group is manifested in other ways, as in that of the esterification of [2,6]-substituted benzoic acids with alcohol and hydrochloric acid (p. 197).

Salicylo-phosphorous Chloride, $C_6H_4\begin{cases}[1]COO\\ [2]O\end{cases}>PCl$, melting at 30° and boiling at 167° (11 mm.), is readily formed when PCl_3 acts upon salicylic acid at 70° (A. 239, 301). All substituted salicylic acids react similarly (B. 30, 221).

Salicylide or *Tetrasalicylide*, $\begin{matrix} O.C_6H_4.COO.C_6H_4.CO \\ CO.C_6H_4O.CO.C_6H_4O \end{matrix}$, melting at 260°, and *Polysalicylide*, $(C_7H_4O_2)x$, melting at 322-325°, are produced when $POCl_3$ acts upon salicylic acid in xylene solution. The two compounds are separated by means of boiling chloroform, with which the tetrasalicylide forms a compound, *Salicylide Chloroform*, $(C_7H_4O_2)_4.2CHCl_3$, crystallizing in beautiful quadratic octahedra, which contain 33 per cent. of chloroform loosely combined as chloroform of crystallization. This body has been used technically in the preparation of pure chloroform (Anschütz, A. **273**, 94). o-Cresotinic acid and the o-haloid salicylic acids behave similarly.

Salicylamide, $HO.C_6H_4.CONH_2$, melts at 138° (B. **24**, 138). *Salicylanilide*, $C_6H_4(OH)CONHC_6H_5$, changes, when heated in dry condition, to *acridone*, $C_6H_4<\begin{matrix} CO \\ NH \end{matrix}>C_6H_4$. It is very probable that it is at first rearranged into phenyl anthranilic acid (p. 213) (B. **29**, 1189). *Salicylo-nitrile*, $HO.C_6H_4.CN$, melting at 98°, is obtained from salicylaldoxime and acetic anhydride (B. **26**, 2621; **27**, R. 134).

Substituted Salicylic Acids.—The 5-derivatives of the mono-substitution products are the most readily prepared. 3-Derivatives are formed simultaneously. Of the disubstituted sâlicylic acids the 3,5-derivatives are made with the most ease. In them the substituents enter the op-position, referred to phenolhydroxyl. 5-*Chlor-*, 5-*brom-*, 5-*iod-*, and 5-*nitro-salicylic acids* melt at 172°, 164°, 196°, and 228°. 3-*Chlor-*, 3-*brom-*, 3-*iod-*, and 3-*nitrosalicylic acids* melt at 178°, 220°, 193°, and 125°. 3,5-*Dichlor-*, 3,5-*dibrom-*, 3,5-*diiod-*, and 3,5-*dinitrosalicylic acids* melt at 214°, 223°, 220–230° with decomposition, and at 173°. An *anhydride*, melting at 187° (B. **30**, 223), has been prepared by the action of the chloride of 3,5-dichlorsalicylic acid upon the silver salt.

m-*Oxybenzoic Acid*, $HO[1]C_6H_4[1]CO_2H$, melts at 200° and sublimes without decomposition. p-*Oxybenzoic Acid*, $HO[4]C_6H_4[1]CO_2H$, melts when anhydrous at 210° with partial decomposition into carbon dioxide and phenol. Its *methyl ester* melts at 131° and boils at 270–280° (B. 27, R. 570). The two acids are obtained from their corresponding amido- and haloid benzoic acids by methods 1 and 2 (p. 221). See p. 223 for the production of p-oxybenzoic acid, together with salicylic acid, by methods 7 and 8. p-Oxybenzoic acid is also obtained from many resins by fusing them with caustic potash. For the behavior of m- and p-oxybenzoic acids with PCl_5, consult p. 224. Compare A. **261**, 236, for the action of chlorine upon the three oxybenzoic acids.

Anisic Acid, p-*Methoxybenzoic Acid*, $CH_3O[4]C_6H_4[1]CO_2H$, melting at 185° and boiling at 280°, is like benzoic and salicylic acids, one of the acids which has been long known. It is isomeric with methyl salicylic ester, and the other monomethyl derivatives of the oxybenzoic acids in general, as well as with the oxyphenylacetic acids. Anisic acid is easily obtained, hence numerous transposition-products of it are known. It is prepared by oxidizing *anethol*, the chief ingredient of anise oil, and other ethereal oils containing anethol (see this), with dilute nitric acid or with a chromic acid mixture.

History.—Cahours (1839) discovered anisic acid when he oxidized anise oil (A. **41**, 66). Kolbe at first considered it methoxybenzoic acid, because when it was distilled with caustic baryta it broke down into CO_2 and *anisol* (p. 146). Saytzew (1863) found that when anisic acid was heated with hydriodic acid it yielded an acid different from salicylic acid, yet isomeric with the latter (A. **127**, 129). This was subsequently found to be p-oxybenzoic acid. In 1867 Ladenburg showed that anisic acid could be prepared by saponifying the dimethyl ether-ester of p-oxybenzoic acid (A. **141**, 241).

Oxytoluic Acids or Cresotinic Acids, $CH_3.C_6H_3(OH).CO_2H$.—The ten possible isomerides are known (B. **16**, 1966). They are isomeric with the three oxyphenylacetic acids (p. 226), the three oxymethylbenzoic acids or benzyl alcohol carboxylic acids, and phenyl glycollic acid or mandelic acid. They have been prepared from the toluic acids by methods 1 and 2, from the oxyaldehydes by method 5, and from the cresols by methods 7 and 8 (p. 222).

3-, 4-, 5-, and 6-Methylhomosalicylic Acids melt at 163°, 177°, 151°, and 168°.
2-, 4-, 5-, and 6-Methylhomo-m-oxybenzoic Acids melt at 183°, 206°, 208°, and 172°.
2- and 3-Methylhomo-p-oxybenzoic Acids melt at 177° and 172°.

Those isomerides containing the hydroxyl-group in the ortho-position with reference to carboxyl, are colored violet by ferric chloride, just like salicylic acid. They dissolve easily in cold chloroform and are volatile with steam. See p. 224 for their behavior toward PCl_5, PCl_3, $POCl_3$, etc. 3-*Methylhomosalicylic acid* yields an o-***homo-salicylide-*** or o-*cresotide-chloroform* (A. **273**, 88) similar to *salicylide-chloroform*. 5-Methyl-m-oxybenzoic acid, prepared synthetically by the action of baryta-water upon acetone oxalic ester (B. **22**, 3271), yields by nitration *nitrococcic acid* or 2,4,6-*trinitro*-m-*oxy*-m-*toluic acid*, melting at 180°, which is also formed when carminic acid (see this), the dye of red cochineal, is oxidized (B. **26**, 2648). When the three isomeric cresotinic acids, or, better, their dibrom-substitution products are reduced with sodium and amyl alcohol, the ring is ruptured and α-, β-, and γ-methylpimelic acids are produced (A. **295**, 173; compare p. 47).

o- and p-*Oxymesitylenic Acids*, $HO.C_6H_2(CH_3)_2CO_2H$, melt at 179° and 223° (A. **206**, 197).

Di- and tri-methyloxybenzoic acids (B. **21**, 884), as well as ethylmethyloxybenzoic acids (A. **195**, 284), are also known. The corresponding isopropyloxybenzoic acids—*Thymo-* and *iso oxycumic acids*, melting at 142° and 94° (B. **19**, 3307)—result upon fusing carvacrol and thymol (p. 144) with caustic potash.

Different isomeric p-methylisopropyloxybenzoic acids, $(CH_3)(C_3H_7)C_6H_2(OH)COOH$: *thymotic* and *carvacrotinic acids* have been made by introducing the CO_2 group into thymol and carvacrol. See B. **28**, 2795 for the derivatives of thymotic acid.

The *oxyphenyl fatty acids* attach themselves to the alkyl-substituted oxybenzoic acids. They are produced (1) by diazotizing the corresponding amidophenyl-fatty acids and then decomposing the diazo derivatives with boiling water; (2) by saponifying the oxybenzyl cyanides.

The o-oxyacids, in which the phenol hydroxyl-group occupies the γ- or δ-position with reference to the carboxyl-group, are, in contrast to the corresponding o-amido-fatty acids (p. 214), capable of existing, but when heated they part with water and yield γ- and δ-lactones (1, 334, 345, 346).

The *oxyphenylacetic acids*, $HO.C_6H_4.CH_2.CO_2H$, are isomeric with the ten oxytoluic acids (see these), with the three oxymethylbenzoic acids, and with the mandelic acids. o-Oxyphenylacetic acid, bearing close relationship to oxindol (p. 214) and isatin (see this), is also obtained from o-oxymandelic acid by reduction with hydriodic acid. Ferric chloride colors it violet. It passes into its lactone (see below) when it is heated. p-*Oxyphenylacetic Acid* occurs in urine, and arises from the decomposition of albuminous bodies as well as in that of *sinalbin*, occurring in the seeds of white mustard (B. **22**, 2137).

o,- m-, and p-*Oxyphenylacetic Acids* melt at 137°, 129°, and 148°. m- and p-*Oxyphenylacetonitrile* melt at 52° and 69° (B. **22**, 2139).

Oxyphenylpropionic Acids.—Four of the six theoretically possible acids are known.

Phloretic Acid, p-*Oxyhydratropic Acid*, $HO[4]C_6H_4[1]CH<^{CO_2H}_{CH_3}$, melting at 129°, is formed, together with phloroglucin, when phloretine (the phloroglucin ester of phloretic acid) is digested with potassium hydroxide. It has been prepared synthetically from p-amidohydrocinnamic acid (p. 214). Ferric chloride colors its solution green. Baryta decomposes it into ethyl phenol; fusion with potassium hydroxide produces paraoxybenzoic acid.

Phloretine, *Monophloreticphloroglucin Ester*, $(HO)_2C_6H_3O.CO.CH(CH_3).C_6H_4OH$, melts at 254° (B. **27**, 1631, 2686). See *phlorizine*.

Hydrocoumaric Acids, or **β-Phenolpropionic Acids**, $HO.C_6H_4.CH_2.CH_2.CO_2H$, result when the corresponding coumaric acids, the oxycinnamic acids, or β-oxyphenylacrylic acids are reduced with sodium amalgam.

o-Hydrocoumaric Acid, or ***Melilotic Acid***, **melting at 81°, occurs free and in combination with coumarin, the lactone of o-oxycinnamic acid, in the yellow melilot (*Melilotus***

officinalis). It is produced by the action of sodium amalgam upon coumarin. Ferric chloride imparts a bluish color to the solution. When distilled, it passes into its lactone—hydrocoumarin. It yields salicylic acid when it is fused with caustic potash.

m- and p-*Hydrocoumaric Acids* melt at 111° and 128°. p-Hydrocoumaric acid is also produced in the decay of tyrosine.

γ- and δ-**Lactones** of o-oxyphenyl-fatty acids are produced when these acids are distilled. They correspond to the γ- and δ-lactams described on p. 214.

o-*Oxyphenylacetic Acid Lactone*, $C_6H_4\left\{\begin{matrix}[1]CH_2.CO\\ [2]O\text{———}\end{matrix}\right.$, melts at 49° and boils at 236° (B. 17, 975).

Hydrocoumarin, *β-o-Oxyphenylpropionic Acid Lactone*, $C_6H_4\left\{\begin{matrix}[1]CH_2.CH_2CO\\ [2]O\end{matrix}\right.$, melts at 25° and boils at 272°. When boiled with water it regenerates the acid from which it was produced by distillation.

B. **Dioxymonocarboxylic Acids** are obtained by the same methods which were used in the preparation of the aromatic monocarboxylic acids. The carboxyl group is more readily introduced into the dioxybenzenes than into the monoxybenzenes. This occurs upon heating the bodies with a solution of ammonium or sodium carbonate to 100° or 130° (B. **18**, 3202; **19**, 2318). The dioxybenzoic acids break down, when heated, into carbon dioxide and dioxybenzenes.

Dioxybenzoic Acids.—The six possible isomerides are known. The most important member of this class is—

Protocatechuic Acid, 3,4-*Dioxybenzoic Acid*, $(HO)_2[3,4]C_6H_3[1]\cdot CO_2H + H_2O$, melts when anhydrous at 190°, and decomposes into pyrocatechin and carbonic acid. It occurs in the fruit of *Illicium religiosum*. It has been obtained from many triderivatives of benzene, containing substituents in the 3,4-position with reference to a side-chain, by fusing them with caustic potash—*e. g.*, from the corresponding bromand iod-p-oxybenzoic acids, bromanisic acid, p- and m-cresolsulphonic acid, sulpho-p-, and sulpho-m-oxybenzoic acids, from eugenol, piperic acid (compare also piperonylic acid, p. 228), etc., as well as from various resins (benzoïn, asafœtida, myrrh, and particularly kino) on fusion with potassium or sodium hydroxide. The latter resin readily yields large quantities of the acid (A. **177**, 188). Compare further phloroglucin ethers of protocatechuic acid. It is also produced by the action of bromine upon quinic acid in aqueous solution.

The *two* possible pyrocatechuic monocarboxylic acids are produced when pyrocatechin is heated to 140° with a solution of ammonium carbonate.

Ferric chloride colors the solution green; after the addition of a very dilute soda solution it becomes blue, later red (all derivatives containing the protocatechuic residue, $(OH)_2C_6H_3.C$—B. **14**, 958, react similarly). Ferrous salts color its salt solutions violet. It reduces an ammoniacal silver solution, but not an alkaline copper solution. *Diprotocatechuic Acid*, $C_{14}H_{10}O_7$, is a tannic acid which results on boiling protocatechuic acid with aqueous arsenic acid. It is very similar to common tannic acid, but is colored green by ferric oxide. It forms a compound with p-oxybenzoic acid by the union of equimolecular quantities (A. **134**, 276; **280**, 18).

See naphthalene ring formations for the conversion of substituted protocatechuic acids, by oxidation with nitric acid, into derivatives of β-naphthoquinone.

The phenol ethers of protocatechuic acid are:

$$C_6H_3\left\{\begin{array}{l}[1]CO_2H\\ [3]OCH_3\\ [4]OH\end{array}\right.\quad C_6H_3\left\{\begin{array}{l}[1]CO_2H\\ [3]OH\\ [4]OCH_3\end{array}\right.\quad C_6H_3\left\{\begin{array}{l}[1]CO_2H\\ [3]OCH_3\\ [4]OCH_3\end{array}\right.\quad C_6H_3\left\{\begin{array}{l}[1]CO_2H\\ [3]O\\ [4]O\end{array}\right\rangle CH_2\quad C_6H_3\left\{\begin{array}{l}[1]CO_2H\\ [3]OCH_2\\ [4]OCH_2\end{array}\right.$$

Vanillic Acid — Isovanillic Acid — Veratric Acid — Piperonylic Acid — Ethylene Protocatechuic Acid.

These alkyl- and alkylen-ether acids are formed when protocatechuic acid is treated with CH_3I, CH_2I_2, and $CH_2Br.CH_2Br$ and caustic potash, as well as by oxidizing the corresponding ethers of protocatechuic aldehyde. The protocatechuic acid can be regained from them upon heating with hydrochloric acid to 150°, when the dimethyl ether acid will yield at first the two monomethyl ether acids; whereas the methylene ether, piperonylic acid, separates carbon in addition to protocatechuic acid:

$$CO_2H.C_6H_3{<}^{O}_{O}{>}CH_2 = CO_2H.C_6H_3{<}^{OH}_{OH} + C.$$

The alkyl ether-acids break down into carbon dioxide and alkyl pyrocatechuic ethers when they are heated with lime or baryta.

Vanillic Acid, m-*Methylprotocatechuic Acid*, melting at 211°, sublimes. It is obtained by the energetic oxidation of its aldehyde, vanillin (p. 219), also from coniferine, as well as by the decomposition of *acetvanillic acid*, melting at 142°, the oxidation product of aceteugenol, acetferulic acid, and acethomovanillic acid, when they are treated with potassium permanganate. Its *nitrile* melts at 87° (B. **24**, 3654).

Isovanillic Acid, p-*Methylprotocatechuic Acid*, melts at 250°, and was first obtained from hemipinic acid (see this), or 4,5-dimethoxy-o-phthalic acid upon heating with hydrochloric acid.

Veratric Acid, 3,4-*Dimethoxybenzoic Acid*, melting at 179.5°, occurs, together with *veratrin* (see the alkaloids), in the sabadilla seeds (from *Veratrum Sabadilla*).

Diethylprotocatechuic acid melts at 149°.

Piperonylic Acid, Methylene-protocatechuic acid, melting at 228°, is also formed by oxidizing α-homopiperonylic acid, obtained from safrol, as well as from piperonal and protocatechuic acid (see this). It breaks down when heated with hydrochloric acid (see above). Its *nitrile* melts at 95° (B. **24**, 3656).

Ethylene protocatechuic acid melts at 133°.

The *phloroglucin ethers of protocatechuic acid* are probably certain vegetable substances which, upon fusion with caustic potash, break down into phloroglucin (p. 165) and protocatechuic acid. They are:

Luteolin, $C_{15}H_{10}O_6$ (B. **29**, R. 647, 848), occurs in *Reseda luteola* and crystallizes in yellow needles. Ferric chloride colors it green.

Catechin, $C_{18}H_{18}O_8$ (?), from catechu, and **Maclurin** or **Moringa Tannic Acid**, $C_{13}H_{10}O_6 + H_2O$, from yellow wood, *Morus tinctoria*, are generally included among the tannic acids. *Proteaic Acid*, $C_9H_{10}O_4$, appears to be a homologue of protocatechuic acid. It is present in *Protea mellifera* (B. **29**, R. 415).

Pyrocatechin-o-carboxylic Acid, 2,3-Dioxybenzoic Acid, $(HO)_2C_6H_3CO_2H + 2H_2O$, melts at 199° when anhydrous. It readily breaks down into CO_2 and pyrocatechin, from which it is formed, together with protocatechuic acid, by the action of ammonium carbonate (A. **220**, 116). It also results when 3-iodsalicylic acid is fused with caustic potash.

Resorcinol Monocarboxylic Acids.—There are three. Sym.-dioxybenzoic acid results on heating sym.-disulphobenzoic acid (p. 216) with caustic potash, and the other two acids are produced when resorcinol is treated with ammonium dicarbonate or potassium dicarbonate solution (B. **18**, 1985; **13**, 2379).

The α-compound is not colored by ferric chloride; whereas the β-body is colored a dark red and the γ-modification blue-violet by the same reagent.

α-*Resorcylic Acid*, 3,5-Dioxybenzoic Acid, $(HO)_2C_6H_3CO_2H + 1\frac{1}{2}H_2O$, melts at 233°. It yields *anthrachrysone* (see this) when it is heated with sulphuric acid.

β-*Resorcylic Acid*, 2,4-Dioxybenzoic Acid $+ 3H_2O$, melts in the anhydrous state at 213°. See B. **28**, R. 1051; **29**, R. 30, for the ethers and esters of the acid.

It is converted in glacial acetic acid solution by chlorine into hexachlor-m-diketo-R-hexene (B. **25**, 2687). The *nitrile* melts at 175°.

γ-Resorcylic Acid, 2,6-Dioxybenzoic acid, melts at 148–167° and breaks down into CO_2 and resorcinol.

Gentisinic Acid, **Hydroquinone Carboxylic Acid**, 2,5-*Dioxybenzoic Acid*, melts at 200°, and at 215° breaks down into carbon dioxide and hydroquinone. It was first prepared from gentisin (see this), a xanthone derivative, together with phloroglucin, on fusing it with caustic potash. It is obtained from 5 brom-, 5 iod-, and 5 amidosalicylic acids; also from hydroquinone and from gentisinic aldehyde (B. **14**, 1988). Ferric chloride colors it a deep blue and is decomposed into CO_2 and quinone (B. **18**, 3499).

The **Dioxytoluic Acids**, $(HO)_2C_6H_2(CH_3)CO_2H$, are isomeric with the dioxyphenylacetic acids. The most important of the known acids of this class is *Orsellinic Acid*, 2,6-dioxy-p-toluic acid, which melts at 176° and breaks down into CO_2 and orcinol (p. 162). It is obtained from orsellic acid upon boiling the latter with water, or erythrin with baryta-water. It is colored violet by ferric chloride.

Orsellic Acid, diorsellinic acid or lecanoric acid, $C_{16}H_{14}O_7$, melting at 153°, is an ether-like anhydride of orsellinic acid, $(HO)_2.C_6H_2(CH_3).CO.OC_6H_2(OH)(CH_3)$-$CO_2H$ (?). It is found in different mosses of the varieties Roccella and Lecanora. Boiling water converts it into orsellinic acid.

Erythrin, $C_{20}H_{22}O_{10} + 1\frac{1}{2}H_2O$, Erythrinic Acid, is an ether derivative of di-orsellinic acid and erythrite. It occurs in the lichen *Roccella fuciformis*, which is applied in the manufacture of archil, and is extracted from it by means of milk of lime. When it is boiled with water it breaks up into orsellinic acid and—

Picro-erythrin, $C_{12}H_{16}O_7 + H_2O$, which, boiled with baryta water, yields erythrite, orcin, and carbon dioxide:

$$\text{Erythrin } C_{20}H_{22}O_{10} + H_2O = (HO)_2C_6H_2(CH_3)CO_2H + C_{12}H_{16}O_7 \text{ Picro-erythrin}$$

$$C_{12}H_{16}O_7 + H_2O = (HO)_2C_6H_3CH_3 + CO_2 + C_4H_6(OH)_4 \text{ Erythrol.}$$

Everninic Acid, $C_9H_{10}O_4 = (HO)_2C_6H(CH_3)_2CO_2H$ (?), is produced, together with orsellinic acid, on boiling *evernic acid* (from *Evernia prunastris*) with baryta. It melts at 157°, and is colored violet by ferric chloride.

Dioxydurylic Acid, pseudocumene hydroquinone carboxylic acid, $(HO)_2[2,5]C_6$-$[3,4,6](CH_3)_3CO_2H$, melts at 210° when rapidly heated, and results from the reduction of *Durylic Acid Quinone*, pseudocumene quinone carboxylic acid, $O_2[2,5]C_6[3,4,6]$-$(CH_3)_3CO_2H$, which decomposes at 130°, and is obtained by the action of ferric chloride upon a hydrochloric acid solution of diamidodurylic acid (A. **237**, 11).

Dioxyphenyl-fatty Acids.—Certain dioxyphenylacetic acids and dioxyphenylpropionic acids in this group are interesting.

α-**Homoprotocatechuic Acid** and its ether-acids have their side-groups occupying the same positions as those of protocatechuic acid and its ether-acids:

$$C_6H_3\begin{cases}CH_2.CO_2H & (1)\\ OH & (3)\\ OH & (4)\end{cases} \qquad C_6H_3\begin{cases}CH_2.CO_2H & (1)\\ O.CH_3 & (3)\\ OH & (4)\end{cases} \qquad C_6H_3\begin{cases}[1]CH_2.CO_2H\\ [3]O \\ [4]O \end{cases}\!\!>CH_2$$

α-Homoprotocatechuic Acid, m. p. 127° — α-Homovanillic Acid, m. p. 142° — α-Homopiperonylic Acid, m. p. 127°.

The acet-*α*-homovanillic acid and *α*-homopiperonylic acid result in the moderated oxidation of aceteugenol (see this) and safrol (see this) with $KMnO_4$. The former melts at 140° and is converted by caustic soda into *α*-homovanillic acid, which hydrochloric acid, at 180°, changes to *α*-homoprotocatechuic acid (B. **10**, 207; **24**, 2882).

Symmetrical Dioxyphenyl-acetic Acid, $(HO)_2[3,5]C_6H_3[1]CH_2.CO_2H + H_2O$, melts at 54°.

The triethyl ester, obtained from the dicarboxylic acid derived from this acid, is produced by the condensation of acetone dicarboxylic ester with sodium. It melts at 98° and yields dioxyphenyl-acetic acid upon saponification. It yields orcin when its silver salt is heated.

Hydrocaffeïc Acid, or *β*-3,4-*dioxyphenylpropionic acid*, corresponds, like *α*-homoprotocatechuic acid, with the same arrangement of the substituting groups as in protocatechuic acid, to—

$C_6H_3\begin{cases}{[1]}CH_2.CH_2.CO_2H\\ {[3]}OCH_3\\ {[4]}OCH_3\end{cases}$	$C_6H_3\begin{cases}{[1]}CH_2.CH_2.CO_2H\\ {[3]}OCH_3\\ {[4]}OH\end{cases}$	$C_6H_3\begin{cases}{[1]}CH_2.CH_2.CO_2H\\ {[3]}OH\\ {[4]}OCH_3\end{cases}$	$C_6H_3\begin{cases}{[1]}CH_2.CH_2.CO_2H\\ {[3]}O\\ {[4]}O\end{cases}\!\!>CH_2$
Hydrocaffeïc Dimethyl Ether Acid, m. p. 96°	Hydroferulic Acid, m. p. 89°	Hydroisoferulic Acid, m. p. 164°	Hydrocaffeïc Methylene Ether Acid, m. p. 84°.

Hydrocaffeïc acid itself and its ether-acids are formed from the corresponding [3,4]-dioxycinnamic or caffeïc acid, and their derivatives, ferulic and isoferulic acids, by reduction with sodium amalgam (B. **11**, 650; **13**, 758). The methylene ether-acid is also produced by oxidizing β-hydropiperic acid (see this) (B. **20**, 421). Ferric chloride colors hydrocaffeïc acid the same as it does protocatechuic acid (p. 227).

Hydro-umbellic Acid, β-2,4-*dioxyphenylpropionic acid*, $(HO)_2[2,4]C_6H_3.CH_2.CH_2.CO_2H$, decomposes at 110°. It is obtained from umbelliferon, the δ-lactone of [2,4]-dioxycinnamic acid, by the action of sodium amalgam. Ferric chloride colors it green.

Trioxybenzoic acids, $(HO)_3C_6H_2CO_2H$. Three of the six possible isomerides are known. The most important is—

Gallic Acid, $(HO)_3[3,4,5]C_6H_2CO_2H + H_2O$. It melts and decomposes about 220° into CO_2 and pyrogallol. It occurs free in tea, in the fruit of *Cæsalpina coriaria* (Divi-divi), in mangoes, and in various other plants. It is obtained from the ordinary tannic acid (tannin) by boiling it with dilute acids. It is prepared artificially from brom-s-m-dioxybenzoic acid and brom-protocatechuic acid when fused with potassium hydroxide.

Gallic acid crystallizes in fine, silky needles. It dissolves with difficulty in cold water, but readily in hot water, alcohol, and ether. It has a faintly acid, astringent taste. It reduces both gold and silver salts (hence its application in photography). Ferric chloride throws down a blackish-blue precipitate in its solutions.

The solutions of its alkali salts absorb oxygen when exposed to the air, and, in consequence, become brown in color.

Rufigallic Acid, a derivative of anthracene (see this), is obtained by heating gallic acid with sulphuric acid.

Oxidizing agents, such as arsenic acid and iodine, convert gallic into *Ellagic Acid*, probably a fluorene derivative.

In alkaline solution gallic acid is converted into *galloflavin* (see this), a yellow dye of the xanthone group. Hydrochloric acid and potassium chlorate decompose the acid into isotrichlorglyceric acid or trichlorpyroracemic acid (11, 45).

Basic Bismuth Gallate, $(HO)_3C_6H_2CO_2Bi(OH)_2$, under the name *dermatol*, is applied as an odorless drying antiseptic.

Ethyl Gallic Ester, $(HO)_3C_6H_2CO_2C_2H_5$, melts at 141°, when anhydrous. *Trimethyl-* and *triethyl gallic ether-acids*, $(R'O)_3C_6H_2CO_2H$, melt at 168° and 112°. *Methylene methyl gallic ether-acid, myristicinic acid*, $(CH_3O)(CH_2O_2).C_6H_2CO_2H$, melts at 130–135° (B. **24**, 3821) when it is anhydrous. *Triacetyl Gallic Acid* melts with decomposition at 170°. *Gallic Acid Anilide*, Gallanol, has been used in medicine. This is true also of *dibromgallic acid*, or *gallobromol*, melting at 140°.

Pyrogallol-carboxylic Acid, $(HO)_3[2,3,4]$-$C_6H_2CO_2H + \frac{1}{3}H_2O$, is prepared by heating pyrogallol with potassium bicarbonate (B. **18**, 3205). It decomposes at 195–200°, but sublimes without decomposition in a current of carbon dioxide. Ferric chloride colors it violet. *Triethyl-pyrogallol-carboxylic Acid*, $C_6H_2(O.C_2H_5)_3.CO_2H$, melts at 105°. It results in the oxidation of triethyldaphnetic acid (see this).

Phloroglucin Carboxylic Acid, $(HO)_3[2,4,6]C_6H_2CO_2H + H_2O$, **decomposes even at 100°, also when boiled with water, into carbon dioxide and phloroglucin, from which it is obtained by boiling with a potassium carbonate solution (B. 18, 1323).**

Triethyloxyhydroquinone Ether-acid, $(C_2H_5O)_3[2,4,5]C_6H_2CO_2H$, melting at 134°, results upon treating α- or β-æsculetine triethyl ether-acid with potassium permanganate (B. 16, 2113).

Asaronic Acid and *Syringaic Acid* (p. 220) are methyl ether-acids, derived from trioxybenzoïc acids.

Iridic Acid, α-homodimethyl gallic ether-acid, $(CH_3O)_2(HO)[3,4,5]C_6H_2CH_2CO_2H$, melting at 118°, is produced along with formic acid and iretol when irigenine is decomposed with baryta-water (B. 26, 2015).

Addendum: **Tannic Acids.**—The tannins or tannic acids are substances widely disseminated in the vegetable kingdom. They are soluble in water, possess an acid, astringent taste, are colored dark blue or green (ink) by ferrous salts, precipitate gelatine, and enter into combination (leather) with animal hides (gelatine). Hence they are employed in the manufacture of leather, and for the preparation of ink. They are precipitated from their aqueous solutions by neutral acetate of lead.

Some tannic acids appear to be glucosides of gallic acid—*i. e.*, ethereal compounds of the same with various sugars. They decompose into gallic acid and grape sugar upon boiling with dilute acids. Others contain phloroglucin instead of grape sugar. Common tannic acid, tannin, appears to be, at least in a pure state, not a glucoside but a digallic acid.

When the tannic acids are fused with potassium hydroxide they yield mostly protocatechuic acid and phloroglucin.

Tannic Acid, Tannin, Digallic Acid, $C_{14}H_{10}O_9 + 2H_2O$, occurs in large quantity (upward of 50 per cent.), in gall-nuts (pathological concretions upon the different oak species, *Quercus infectoria*, produced by the sting of insects); in sumach (*Rhus coriaria*), in tea, and in other plants. It is prepared artificially by heating gallic acid with phosphorus oxychloride to 130°, or by boiling with dilute arsenic acid. Conversely, it passes, on boiling with dilute acids or alkalies, into gallic acid:

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5.$$

Pure tannin must, therefore, be considered a digallic acid (B. 17, 1478).

Tannin is best obtained from gall-nuts. The latter are finely divided and extracted with ether and alcohol. The solution separates into two layers, the lower of which is aqueous and contains tannin chiefly, and this is obtained by evaporation.

Pure tannic acid is a colorless, shining, amorphous mass, very soluble in water, slightly in alcohol, and almost insoluble in ether. Many salts —*e. g.*, sodium chloride—precipitate it from its aqueous solutions, and it can also be removed from the latter by shaking with acetic ether. It reacts acid and is colored dark blue by ferric chloride (ink); gelatine precipitates it. Quantitative methods of estimating tannin are based on this behavior.

The *penta-acetate*, $C_{14}O_5(C_2H_3O)_5O_9$, heated to 210°, decomposes with formation of pyrogallol (p. 164).

Gallyl-gallic Acid, $C_{14}H_{10}O_9$, a keto-tannic acid, forms an oxime and phenylhydrazone. See B. 22, R. 754; 23, R. 24.

The other tannic acids found in plants have been but little investigated; we may mention—

Kino-tannin, which constitutes the chief ingredient of kino, the dried juice of *Pterocarpus erinaceus* and *Coccoloba uvifera*. Its solution is colored green by ferric salts. It yields phloroglucin on fusion with potassium hydroxide.

Catechu-Tannin occurs in catechin, the extract of *Mimosa Catechu*. Ferric salts color it a dirty green (p. 227). *Catechin* or *Catechinic Acid*, $C_{21}H_{20}O_9 + 5H_2O$, is also present in catechu. It crystallizes in shining needles.

Moringa-Tannin, $C_{13}H_{10}O_6 + H_2O$, *Maclurin*, is found in yellow wood (*Morus tinctoria*), from which it may be extracted (along with morin) with hot water. When the solution cools morin separates out; maclurin is precipitated from the concentrated liquid by hydrochloric acid, in the form of a yellow crystalline powder, soluble in water and alcohol. Ferric salts impart a greenish-black color to its solutions. When fused with caustic potash it yields protocatechuic acid and phloroglucin. It forms pentacidyl derivatives (Ch. C. 1897, 466).

Morin, $C_{13}H_8O_6 + 2H_2O$, decomposes into phloroglucin and resorcin. Nitric acid oxidizes it to β-resorcylic acid. Consult B. **29**, R. 646, for its constitution.

The *Tannin* of *Coffee*, $C_{30}H_{18}O_{16}$, occurs in coffee beans and Paraguay tea. Gelatine does not precipitate its solutions. Ferric chloride gives them a green color. It decomposes into caffeïc acid (see this) and sugar when boiled with potassium hydroxide. Protocatechuic acid is produced when it is fused with potassium hydroxide.

The *Tannin* of *Oak* is found in the bark (together with gallic acid, ellagic acid, quercite). It has the formula $C_{19}H_{16}O_{10}$, and is a red powder, not very soluble in cold water, but more readily in acetic ether. Ferric chloride colors its solution dark blue. Boiling, dilute sulphuric acid converts it into the so-called *oak red* (phlobaphene), $C_{38}H_{26}O_{17}$ (?).

The *Tannin* found in the quinine barks is combined with the quinia-alkaloids. It closely resembles ordinary tannic acid, but is colored green by ferric salts. When boiled with dilute acids it breaks up into sugar and *quina-red*, an amorphous brown substance, yielding protocatechuic acid and acetic acid on fusion with potassium hydroxide.

2. POLYHYDRIC AROMATIC ALCOHOLS, IN WHICH ONLY ONE HYDROXYL IS PRESENT IN EACH SIDE-CHAIN, AND THEIR OXIDATION PRODUCTS.

1. DI- AND TRIHYDRIC AROMATIC ALCOHOLS.

Xylylene Alcohols, $C_6H_4(CH_2OH)_2$.—The three isomerides are obtained from the three corresponding xylylene chlorides or bromides by boiling with a soda solution. The *ortho* (1,2), called **Phthalyl alcohol**, is obtained also from phthalic acid chloride by reduction in glacial acetic acid with a large excess of sodium amalgam (B. **12**, 646).

1,2-*Phthalyl Alcohol* melts at 62°; dichloride melts at 55°; the dibromide melts at 95°.

1,3-*Xylylene Alcohol* melts at 46°; dichloride melts at 34°; the dibromide melts at 77°.

1,4-*Xylylene Alcohol* melts at 112°; dichloride melts at 100°; the dibromide melts at 143°.

The three chlorides are formed when the xylenes are heated to 150° with PCl_5 (B. **19**, R. 24). The bromides are produced when bromine acts upon boiling xylenes (B. **18**, 1281), or upon the latter in sunlight (B. **18**, 1278). *Tetrachlorxylylene Oxide*, $C_6Cl_4(CH_2)_2O$, melts at 218° (A. **238**, 331). o-*Xylylene Sulphide*, $C_6H_4(CH_2)_2S$ (B. **17**, 1824).

o-*Xylylendiamine*, $C_6H_4[1,2](CH_2NH_2)_2$, is a liquid. It results when potassium phthalimide acts upon o-xylylene bromide (B. **21**, 578), as well as by the reduction of phthalazine (p. 233). Upon heating, its chloride yields:

o-*Xylylenimine*, dihydroisoindol, $C_6H_4(CH_2)_2NH$, boiling at 213°. It also results in the reduction of chlorphthalazine (B. **26**, 2212).

Pseudocumenyl Glycol, $CH_3[1]C_6H_3[2,4](CH_2OH)_2$, melts at 77° (B. **19**, 867).

Mesitylene Glycol, $CH_3[1]C_6H_3[3,5](CH_2OH)_2$, boils at 190° (20 mm.).

ω_2-*Diamidomesitylene*, $CH_3 . C_6H_3(CH_2NH_2)_2$, boils at 268° (B. **25**, 3017).

Mesitylene Glycerol, Mesicerine, $C_6H_3[1,3,5](CH_2OH)_3$, is a thick liquid (B. 16, 2509).

p-*Di-a-oxethyl Benzene*, $C_6H_4[CH(OH)CH_3]_2$, is a liquid obtained from p-diacetyl benzene (B. 27, 2527).

The dihydric aromatic alcohols with the hydroxyl groups attached to two side-chains give rise to nine classes of oxidation-products, just as in the case of the aliphatic glycols (I, 290).

2. ALDEHYDE ALCOHOLS.

In this connection mention may be made of *hydrophthalide*, $C_6H_4\left\{\begin{matrix}[1]CH_2-O \\ [2]CH\angle OH\end{matrix}\right.$, the reduction product of phthalide. It is a syrup, soluble in water. *Dimethylhydrophthalide*, $C_6H_4\left\{\begin{matrix}[1]C(CH_3)_2 \\ [2]CH(OH)\end{matrix}\right\rangle O$, the reduction-product of dimethylphthalide, melts at 89° (A. 248, 61).

3. AROMATIC DIALDEHYDES.

Phthalic Acid Aldehydes, $C_6H_4(CHO)_2$, corresponding to the three phthalic acids are obtained, like benzaldehyde from benzal chloride, by heating the xylylene tetrachlorides with water. o-Xylylene tetrachloride, or, better, o-xylylene tetrabromide and hydrazine yield *phthalazine*, $C_6H_4\left\{\begin{matrix}CH:N \\ CH:N\end{matrix}\right.$ (B. 28, 1830).

o-*Phthalaldehyde* melts at 52°; the *dioxime* melts at 245° (B. 20, 509).

Isophthalaldehyde melts at 89°; the *dioxime* melts at 180° (B. 20, 2005).

Terephthalaldehyde melts at 114°; the *dioxime* melts at 200° (B. 16, 2995).

The o-, m-, and p-xylylene tetrachlorides, $C_6H_4(CHCl_2)_2$, corresponding to the aldehydes, are prepared by heating the three xylenes with PCl_5 to 150–190°.

The o-*body* melts at 89° and boils at 273°.

The m-*body* boils at 273°, and the p-compound melts at 93°.

ω-*Tetrabrom*-o-*xylene* melts at 116° (B. 28, 1830).

Oxydialdehydes are produced together with and from the oxymonaldehydes by means of Reimer's reaction (p. 218).

Thymodialdehyde, $HO.C_6H(CH_3)(C_3H_7)(CHO)_2$, melts at 79° (B. 16, 2104).

Resorcindialdehyde, $(HO)_2.C_6H_2(CHO)_2$, melts at 127° (B. 10, 2212).

α- and β-Orcendialdehydes, $(HO)_2C_6H(CH_3)(CHO)_2$, melt at 118° and 168° (B. 12, 1003).

α- and β-Oxyisophthalaldehyde, $(HO)[4]C_6H_3(CHO)_2$ and $HO[2]C_6H_3(CHO)_2$, melt at 108° and 88° (B. 15, 2022).

4. DI- AND TRIKETONES.

Only one acidyl group can be introduced into benzene even by means of the aluminium chloride synthesis.

p-**Diacetylbenzene**, $C_6H_4[1,4](COCH_3)_2$, melting at 114°, is formed by the action of dilute sulphuric acid upon terephthalyl dimalonic ester (B. 27, 2527). *Diethyl Terephthalyl*, $C_6H_4(COC_2H_5)_2$ (B. 19, 1850). *Triacetyl Benzene*, $C_6H_3[1,3,5](COCH_3)_3$, melting at 163°, is formed by the benzene ring formation from formyl acetone (I, 319; II, 42). In the benzene homologues containing methyl-groups in the meta-positions it is an easy matter, aided by Al_2Cl_6, to introduce acetyl residues between every two such methyl-groups. Thus, mesitylene, durene, and isodurene have given:

Diacetyl Mesitylene, $C_6H(CH_3)_3(COCH_3)_2$, melting at 46° and boiling at 310°; **diacetyl durene**, melting at 178° and boiling at 323–326°, and **diacetyl isodurene**, melting at 121° and boiling at 312–317° (B. 28, 3213; 29, 1413).

5. ALCOHOL CARBOXYLIC ACIDS.

Oxymethylbenzoic Acids, Carbinolbenzoic Acids.—These are three possible isomerides, and all of them have been prepared. They are isomeric with mandelic acid and the oxytoluic acids. o-Oxymethyl-

benzoic acid passes quite readily into the corresponding γ-lactone, *phthalide*. Phthalide and meconine are the first lactones with which organic chemistry was enriched.

o-**Oxymethylbenzoic Acid,** *Benzylalcohol-o-carboxylic acid,* $C_6H_4\left\{\begin{matrix}[1]CO_2H\\ [2]CH_2OH\end{matrix}\right.$, melts at 120°, loses water and becomes phthalide, from which it is obtained by dissolving in caustic alkali and then precipitating with mineral acids.

Phthalide, o-*Oxymethylbenzoic Acid Lactone,* $C_6H_4\left\{\begin{matrix}[1]CO\\ [2]CH_2\end{matrix}\right\rangle O$, melting at 83° and boiling at 290°, was first made from o-phthalic acid. It is formed (1) by heating o-oxymethylbenzoic acid or by allowing it to stand in contact with water (B. **25**, 524); (2) by the reduction of phthalide chloride with zinc and hydrochloric acid (B. **10**, 1445); (3) by the reduction of phthalic anhydride in acetic acid solution with zinc-dust (B. **17**, 2178); (4) by the action of bromine vapor upon orthotoluic acid at 130–140°; (5) from xylylene dichloride upon boiling with water and lead nitrate; (6) by decomposing nitrosophthalimidine obtained from phthalimide with caustic potash (A. **247**, 291); or (7) by treating o-cyanbenzyl chloride in glacial acetic acid with hydrochloric acid at 100° (B. **25**, 3021).

It is reduced to orthotoluic acid on boiling with hydriodic acid. Potassium permanganate oxidizes it to phthalic acid. See also phthalaldehydic acid (p. 236), phthalic acid and ω-cyan-o-toluic acid (p. 244). Phenylhydrazine adds itself to phthalide (B. **26**, 1273).

Numerous derivatives have been obtained from o-oxymethylbenzoic acid, some of which, like the acid itself, change over to heterocyclic compounds.

o-**Chlormethylbenzoic Acid,** $Cl.CH_2[2]C_6H_4CO_2H$. The free acid is not known. Its *ethyl ester* results from the action of alcohol upon its chloride.

It boils at 141° (12 mm.), and also without decomposition at 245° (760 mm.).

o-**Chlormethyl Benzoyl Chloride, Phthalide Chloride,** $ClCH_2[2]C_6H_4.COCl$, boiling at 135° (12 mm.), results when PCl_5 acts upon phthalide at 55–60°.

o-**Chlormethylbenzamide,** $ClCH_2[2]C_6H_4.CONH_2$, melts with decomposition at 190° (see pseudophthalimidine). It is produced on conducting dry ammonia into an ethereal solution of phthalide chloride solution, and by the action of sulphuric acid upon its nitrile.

o-**Chlormethyl Benzanilide,** $Cl.CH_2[2]C_6H_4CONHC_6H_5$, melts at 115°.

o-**Chlormethyl Benzonitrile,** o-**Cyanbenzyl Chloride,** $Cl.CH_2[2]C_6H_4CN$, melting at 252°, is formed upon conducting chlorine into boiling o-tolunitrile (p. 203) (B. **20**, 2222). The corresponding o-*Cyanbenzyl alcohol* is known only in its ethers (B. **25**, 3018).

Phthalide yields the base **Phthalimidine,** $C_6H_4\left\{\begin{matrix}[1]CO\\ [2]CH_2\end{matrix}\right\rangle NH$, when it is heated in an atmosphere of ammonia. It can also be very readily obtained by reducing phthalimide with tin and hydrochloric acid (A. **247**, 291); from o-cyanbenzylamine with nitrous acid, and from phthalide chloride by the action of alcohol and ammonia. It melts at 150° and boils at 337°.

Nitrosophthalimidine, $C_8H_6ON.NO$, melts at 156°. *Pseudophthalimidine,* $C_6H_4\left\{\begin{matrix}[1]C=\!=\!=NH\\ [2]CH_2\!-\!>O\end{matrix}\right.$, is an oil. In contact with water it is resolved into phthalide and ammonia. Its hydrochloride is formed when o-chlormethyl-benzamide is heated to 130°–140°.

Phthalide Anil, *Phenylphthalimidine,* $C_6H_4\left\{\begin{matrix}[1]CO\\ [2]CH_2\end{matrix}\right\rangle NC_6H_5$, melting at 160°,

results on heating phthalide and aniline to 200–220°, upon reducing phthalanil with tin and hydrochloric acid, and by distilling o-chlormethylbenzanilide under diminished pressure. **o-Cyanbenzylamine**, $NH_2 . CH_2[2]C_6H_4CN$, is a colorless oil, which becomes crystalline. It is formed when o-cyanbenzyl chloride acts upon potassium phthalimide (B. **20**, 2233).

Thiophthalide, $C_6H_4\left\{\begin{matrix}[1]CO\\ [2]CH_2\end{matrix}\right.>S$, melts at 60° (A. **257**, 298), and—

Selenophthalide, $C_6H_4\left\{\begin{matrix}[1]CO\\ [2]CH_2\end{matrix}\right.>Se$, melts at 58° (B. **24**, 2596). Phthalides, substituted in the benzene nucleus, are also known; they have been mostly obtained from substituted o-phthalic acids. Mention may be made of:

p-Nitrophthalide, $NO_2C_6H_3\left\{\begin{matrix}[1]CO\\ [2]CH_2\end{matrix}\right.>O$, melting at 135°. It is produced when chromic acid and glacial acetic acid act upon o-nitronaphthalene (A. **202**, 219).

p-Oxyphthalide, $HO . C_6H_3\left\{\begin{matrix}[1]CO\\ [2]CH_2\end{matrix}\right.>O$, melting at 222° (A. **233**, 235), is obtained from p-oxy-o-phthalic acid.

Meconine, 5,6-*Dimethoxyphthalide*, $(CH_3O)_2[5,6]C_6H_2\left\{\begin{matrix}[1]CO\\ [2]CH_2\end{matrix}\right.>O$, melting at 102°, is the lactone of meconinic acid, which is only stable in the form of its salts. Its name is derived from the Greek word μήκων, signifying *poppy*.

Meconine occurs already formed in opium, where Couerbe discovered it in 1832, and is obtained on boiling narcotine with water (Wöhler and Liebig, 1832). It may be formed from opianic acid (p. 237), the corresponding aldehyde acid, just like phthalide from phthalaldehydic acid, by reduction with sodium amalgam and precipitation with acids. It was the first lactone known to chemistry. It dissolves in the alkalies, yielding salts of meconinic acid. In the same manner that phthalimide yields phthalide (p. 234), hemipinimide furnishes ψ-meconine, and not meconine (B. **20**, 883).

$C_6H_4\left\{\begin{matrix}[1]CO\\ [2]CH_2\end{matrix}\right.>O$	$C_6H_4\left\{\begin{matrix}[1]CHO\\ [2]CO_2H\end{matrix}\right.$	$(CH_3O)_2C_6H_2\left\{\begin{matrix}CO\\ CH_2\end{matrix}\right.>O$	$(CH_3O)_2C_6H_2\left\{\begin{matrix}CHO\\ CO_2H\end{matrix}\right.$
Phthalide	Phthalaldehydic Acid	Meconine	Opianic Acid.

ψ-Meconine, 3,4-*Dimethoxyphthalide*, $(CH_3O)_2[3,4]C_6H_2\left\{\begin{matrix}[1]CO\\ [2]CH_2\end{matrix}\right.>O$, melts at 132°. It is made from hemipinimide, just as phthalide is formed from phthalimide (B. **20**, 884).

o-α-**Oxyethylbenzoic Acid Lactone**, α-*Methylphthalide*, $C_6H_4\left\{\begin{matrix}[1]CO\\ [2]CH\end{matrix}\right.>O$, boils at 275°. It is formed in the reduction of acetophenone-o-carboxylic acid (p. 238) with sodium amalgam. Hydriodic acid and phosphorus reduce it to o-ethylbenzoic acid (B. **29**, 2533).

Dimethyl Phthalide, o-β-*oxyisopropylbenzoic acid lactone*, $C_6H_4\left\{\begin{matrix}[1]CO>O\\ [2]C<(CH_3)_2\end{matrix}\right.$, melting at 67° and boiling at 270°, was made by the action of zinc-dust and methyl iodide upon phthalic anhydride (A. **248**, 57).

m-Oxymethylbenzoic Acid is only known in the form of its alcohol anhydride, $O[CH_2[3]C_6H_4COOH]_2$, melting at 180°, which is formed from m-cyanbenzyl chloride, $Cl . CH_2[3]C_6H_4CN$, melting at 67° and boiling at 259°, the reaction-product of chlorine upon m-tolunitrile (p. 203). ω-*Chlor*-m-*toluic Acid* melts at 135°, and **m-Benzylamine Carboxylic Acid**, $NH_2CH_2[3]C_6H_4CO_2H$, melts at 216°.

p-Oxymethylbenzoic Acid, $HO . CH_2[4]C_6H_4CO_2H$, melting at 181°, is obtained (1) from **p-carbinol bromide benzoic acid**, $Br . CH_2[4]C_6H_4 . CO_2H$ (A. **162**, 342); (2) by the action of concentrated sodium hydroxide upon terephthalaldehyde (A. **231**, 372).

p-Cyanbenzyl Alcohol, $HOCH_2[4]C_6H_4CN$, melting at 133°, is prepared from **p-cyanbenzyl chloride**, melting at 79° and boiling at 263°, by the action of potassium

carbonate. **p-Chlormethylbenzamide**, $CH_2Cl[4]C_6H_4CONH_2$, melts at 173°. **p-Chlormethylbenzoic Acid**, $CH_2Cl[4]C_6H_4CO_2H$, melts at 199° (B. **24**, 2416).

m- and p-Oxyisopropylbenzoic Acids, $(CH_3)_2C(OH).C_6H_4.CO_2H$, melting at 123° and 155°, result when m-isocymene (A. **275**, 159), and cymene, from cumic acid, are oxidized with potassium permanganate. The 3-amido-4-oxyisopropylbenzoic acid, derived from the p-acid, changes under the influence of carboxylic anhydrides into *cumazonic acids* (see these).

6. ALDEHYDE ACIDS.

o-Phthalaldehydic acid and 5,6-dimethoxy-o-phthalaldehydic acid, or *opianic acid*, are the most important representatives of this class. In the phthalaldehyde acids the aldehyde group occupies the γ-position with reference to the carboxyl group. Like the aliphatic γ-ketonic acids (the lævulinic acids, 1, 379), the phthalaldehyde acids form monoacetyl derivatives, whose existence and deportment argue more strongly for the γ-oxylactone formula (Liebermann, B. **19**, 765, 2288) than the carboxylic acid formula of such acids:

$$\begin{array}{l} CH_2.CO_2H \\ | \\ CH_2.CO.CH_3 \end{array} \text{ or } \begin{array}{l} CH_2.CO\diagdown_{O} \\ | \qquad\quad\diagup \\ CH_2-C\begin{cases} OH \\ CH_3 \end{cases} \end{array} \qquad C_6H_4\begin{cases}[1]CO_2H \\ [2]CHO\end{cases} \text{ or } C_6H_4\begin{cases}[1]CO \\ \qquad >O \\ [2]CH.OH\end{cases}$$

Lævulinic Acid — o-Phthalaldehydic Acid.

Opianic acid forms two series of esters. Their difference is due to the fact that the one series represents carboxylic esters, while the other series consists of γ-oxylactone esters.

The deportment of the oxime anhydrides of phthalaldehydic acid and opanic acid is worthy of note. They change to the corresponding phthalimides with an appreciable evolution of heat, when they are gently heated. The phthalaldehydoxime anhydridic acid first changes to o cyanbenzoic acid, which yields phthalimide upon fusion. The determination of the heat of combustion of opian-oximic acid anhydride and hemipinimide has shown that in the conversion of the former into the latter the quantity of heat set free (52.6 Cal. for the gram-molecule) was tenfold greater than the molecular rearrangement-energy of allocinnamic into cinnamic acid, and eight times that observed in the conversion of maleïc into fumaric acid (B. **25**, 89).

o-Phthalaldehydic Acid (formulas above), melting at 97°, is formed (1) upon heating bromphthalide (see below) with water; (2) by heating ω-pentachlor-o-xylene and (3) o-cyanbenzal chloride with hydrochloric acid (B. **30**, 3197). Hydrazine converts the acid into *phthalazone* (see this) $C_6H_4\begin{cases}[1]CO-NH \\ \quad\;\; | \qquad\;\; | \\ [2]CH-N\end{cases}$, melting at 183°; phenylhydrazine changes it to *phenylphthalazone*, melting at 105° (B. **26**, 531), and hydroxylamine, in aqueous solution, into **benzaldoxime-o-carboxylic acid**, melting at 120°; while in alcoholic solution the product is **benzaldoxime o-carbonic anhydride**, benzo-ortho-oxazinone, melting at 145°. The latter at 145° rearranges itself with evolution of much heat into o-cyanbenzoic acid, which at more elevated temperatures becomes *phthalimide* (B. **26**, 3264):

$$C_6H_4\begin{cases}[1]COOH \\ [2]CH=NOH\end{cases} \rightarrow C_6H_4\begin{cases}[1]\,COO \\ \qquad\;\; | \\ [2]\,CHN\end{cases} \rightarrow C_6H_4\begin{cases}[1]COOH \\ [2]C\equiv N\end{cases} \rightarrow C_6H_4\begin{cases}[1]CO \\ [2]CO\end{cases}>NH.$$

Benzaldoxime-o-Carboxylic Acid — Benzaldoxime-o-Carboxylic Acid Anhydride — o-Cyanbenzoic Acid — o-Phthalimide.

Methoxyphthalide, *phthalaldehydic methyl ether*, melting at 44°; **ethoxyphthalide** melting at 66°, and **amidophthalide**, *amide of phthalaldehydic acid*, are produced by the action of methyl and ethyl alcohol, and of ammonia upon **bromphthalide, or the**

bromide of phthalaldehydic acid, melting at 85°, produced when bromine vapor acts upon phthalide at 140°. **Aceto-phthalaldehydic acid**, *acetoxyphthalide*, is formed by the interaction of acetic anhydride and phthalaldehydic acid.

Diphthalide Ether, $C_6H_4\left\{\begin{array}{l}[1]CO\\ [2]CH\end{array}\right.\!\!>O\ O<\!\!\left.\begin{array}{l}CO[1]\\ CH[2]\end{array}\right\}C_6H_4$ (with the two CH groups joined through —O—), melting at 221°, is formed from o-phthalaldehydic acid and bromphthalide. In accordance with the double formulation of phthalaldehydic acid (see above) two views may be held in regard to its various derivatives:

$$C_6H_4\left\{\begin{array}{l}[1]COOCH_3\\ [2]CHO\end{array}\right. \quad C_6H_4\left\{\begin{array}{l}[1]CONH_2\\ [2]CHO\end{array}\right. \quad C_6H_4\left\{\begin{array}{l}[1]COBr\\ [2]CHO\end{array}\right. \quad C_6H_4\left\{\begin{array}{l}[1]COOCOCH_3\\ [2]CHO\end{array}\right.$$

$$C_6H_4\left\{\begin{array}{l}[1]CO>O\\ [2]CH-OCH_3\end{array}\right. \quad C_6H_4\left\{\begin{array}{l}[1]CO>O\\ [2]CH-NH_2\end{array}\right. \quad C_6H_4\left\{\begin{array}{l}[1]CO>O\\ [2]CHBr\end{array}\right. \quad C_6H_4\left\{\begin{array}{l}[1]CO>O\\ [2]CH\ OCOCH_3\end{array}\right.$$

Methoxyphthalide   Amidophthalide   Bromphthalide   Acetoxyphthalide.

The idea that acetoxyphthalide and the diphthalide ethers are anhydrides of carboxylic acids is very improbable. Phthalaldehydic acid and opianic acid react especially readily, even in the cold, with amines. Water is eliminated. The resulting bodies dissolve in part very easily in soda, and in part with difficulty, hence are in part derived from the amidophthalide and partly from the imidoaldehydic acid formula (B. **29**, 174, 2030).

$$C_6H_4\left\{\begin{array}{l}[1]CO>O\\ [2]CH-NHR\end{array}\right. \quad \text{and} \quad C_6H_4\left\{\begin{array}{l}[1]COOH\\ [2]CH=NR.\end{array}\right.$$

Phthalaldehyde Chlorides: **Penta-chloride of o-Phthalaldehydic Acid**, n-*Pentachlor-o-xylene*, $CHCl_2[2]C_6H_4CCl_3$, melting at 53°, results when PCl_5 acts upon o-xylene at 140°. **o-Cyanbenzal Chloride**, nitrile of o-phthalaldehyde-chloride acid, $CHCl_2$-$[2]C_6H_4CN$, boiling at 260°, is formed by the action of chlorine upon boiling o-cyantoluene (B. **30**, 3197).

Noropianic Acid, 5,6-*dioxyphthalaldehydic acid*, $(HO)_2C_6H_4(CHO)COOH$, melting at 171°, is obtained from opianic acid, together with isovanillin and carbon dioxide, upon heating with hydriodic acid. It is colored bluish-green by ferric chloride.

Opianic Acid, 5,6-*dimethoxyphthalaldehydic acid*, $(CH_3O)_2[5,6]C_6H_2[2]CHO$.-$CO_2H$, melting at 150°, is produced on oxidizing narcotine with dilute sulphuric acid and MnO_2 (1842, Wöhler and Liebig, A. **44**, 126). Meconine is formed in its reduction. When it is evaporated with caustic potash it changes in part to meconine and partly to hemipinic acid, just as benzaldehyde yields benzyl alcohol and benzoic acid. It is oxidized to hemipinic acid (p. 241). Upon heating with hydrochloric acid there results at first: **5-Methoxy-6-oxyphthalaldehydic acid**, *methyl noropianic acid*, $(CH_3O)[5](HO)[6]$-$C_6H_2(CHO)CO_2H$, melting at 154° (B. **30**, 691), while under more intense heat isovanillin and CO_2 are the products. Concentrated sulphuric acid converts opianic acid into *rufiopin* (see this), a tetraoxyanthraquinone derivative.

Opianic acid behaves toward hydrazine, phenylhydrazine, and hydroxylamine just like phthalaldehydic acid (p. 236). **Dimethoxyphthalazone**, *opiazone*, melts at 162°, when it is anhydrous (B. **27**, 1418). **Phenylopiazone** melts at 175° (B. **19**, 2518). **Opianoximic Acid**, melting at 82°, becomes, on boiling its aqueous solution, the **anhydride of opianoximic acid**, melting at 114°. When this is heated alone, or when its alcoholic solution is boiled, hemipinimide results as a consequence of rearrangement (B. **24**, 3264).

Esters.—Opianic acid forms two series of alkyl esters, corresponding to the carboxylic and to the γ-oxylactone formulas of the acid (p. 236). The one series, the true carboxylic esters, are stable in the presence of water. They are formed by the action of alkyl iodides upon the silver salt or of alcohols upon the chloride of opianic acid.

They manifest the typical aldehyde reactions (B. **29**, R. 507). The second series, the γ-oxylactones or ψ-esters, are formed on boiling opianic acid with alcohols: **Methyl Opianic Ester**, $(CH_3O)_2C_6H_2(CHO)CO_2CH_3$, melts at 82° and boils at 233°

(51 mm.). The **ethyl ester** melts at 64°. **ψ-Methyl Opianic Ester,**

$$(CH_3O)_2C_6H_2\left\{\begin{matrix}CH \\ \quad >O \\ CO-OCH_3\end{matrix}\right.$$

, melts at 103° and boils at 238° (52 mm.). The **ψ-ethyl ester** melts at 92° (B. **25**, R. 907; **26**, R. 700). **Acetyl-opianic Acid** melts at 120° (B. **19**, 2288). **[3]-Nitro-opianic Acid**, melting at 166°, yields by reduction **dimethoxyanthranilcarboxylic acid**, *azoopianic acid*, which upon treatment with acetone and sodium hydroxide forms an indigo derivative (compare anthranil, p. 212). **Pseudo-opianic Acid**, $(CH_3O)_2[3,4]C_6H_2[2](CHO)CO_2H$, melting at 121°, is formed from berberal, an oxidation product of the alkaloid *berberine* (see this), when it is boiled with dilute sulphuric acid. Amidoethylpiperonylcarboxylic anhydride (B. **24**, R. 158) is formed simultaneously. The *oxime*, melting at 124°, is rearranged upon heating into hemipinimide (B. **24**, 3266).

m-Aldehydo-benzoic Acid, *Isophthalaldehydic acid*, $CHO[3]C_6H_4CO_2H$, melts at 165°. **m-Cyanbenzaldehyde** melts at 80°. **m-Cyanbenzal Chloride** boils at 274° (B. **24**, 2416). **p-Aldehydo-benzoic Acid**, *Terephthalaldehydic Acid*, $CHO[4]C_6H_4.CO_2H$, melts at 285°. **p-Cyanbenzaldehyde** melts at 97°. **p-Cyanbenzal Chloride** boils at 275° (B. **24**, 2422).

Mono- and dioxyaldehydo-acids have been obtained from mono- and dioxycarboxylic acids by means of chloroform and caustic alkali (B. **12**, 1334; **16**, 2182).

7. KETONE CARBOXYLIC ACIDS.

o-Acetophenone carboxylic acid is the most important of the aromatic monocarboxylic acids with keto- and carboxyl-groups in different side-chains. In it the γ-position imparts to the keto- and carboxyl groups reactions similar to those manifested by o-phthalaldehydic acid (p. 236). Hence in addition to the carboxylic acid formula we must also consider the γ-oxylactone formula for o-acetophenone carboxylic acid. Its acetyl compound must be viewed as acetyl-γ-oxylactone:

$$C_6H_4\left\{\begin{matrix}[1]COOH \\ [2]COCH_3\end{matrix}\right. \quad \text{or} \quad C_6H_4\left\{\begin{matrix}[1]CO>O \\ [2]C(OH)CH_3\end{matrix}\right. \qquad C_6H_4\left\{\begin{matrix}[1]CO>O \\ [2]C(OCOCH_3)CH_3.\end{matrix}\right.$$

o-Acetophenone Carboxylic Acid, *o-Acetobenzoic Acid*, melting at 115°, is isomeric with benzoyl acetic acid (see this) and tolylglyoxylic acid (see this). It has a sweet taste, and is formed on boiling benzoyl aceto-o-carboxylic acid with water (B. **26**, 705; **29**, 2533). The *acetyl compound* melts at 70° (B. **14**, 921). Hydrazine converts it into *methylphthalazone*, melting at 222° and boiling at 247° (B. **26**, 705). With phenylhydrazine it yields *methyl-n-phenylphthalazone*, melting at 102° (B. **18**, 803). Its ethyl ester and hydroxylamine form an *oxime anhydride*, melting at 158° (B. **16**, 1995).

Various homologous o-acidylbenzoic acids have been obtained by digesting their anhydrides, the alkylidene phthalides, with potassium hydroxide. These anhydrides are produced in the condensation of phthalic anhydride and fatty acids, when water and carbon dioxide are eliminated: **o-butyrophenone carboxylic acid** and **o-isovalerophenone carboxylic acid** melt at 89° and 88° (B. **29**, 1437).

p-Acetophenone Carboxylic Acid melts at 200°. It results from the oxidation of p-β-oxyisopropylbenzoic acid (A. **219**, 260). **p-Cyanacetophenone**, melting at 60°, is made from p-amido-acetophenone (B. **20**, 2955).

Polycarboxylic Acids.—Three varieties are to be distinguished in each group of these acids: those in which all the carboxyl groups are directly joined to the benzene nucleus; those in which these groups are in part joined to the nucleus and are in part present in the side-chains; and, lastly, those in which all of the carboxyl groups are contained in the side-chains—*e. g.*:

$$C_6H_4\left\{\begin{matrix}COOH \\ COOH\end{matrix}\right. \qquad C_6H_4\left\{\begin{matrix}CH_2.CO_2H \\ CO_2H\end{matrix}\right. \qquad C_6H_4\left\{\begin{matrix}CH_2.CO_2H \\ CH_2.CO_2H\end{matrix}\right.$$

Phthalic Acids **Homophthalic Acids** **Phenylene Diacetic Acids.**

8. DICARBOXYLIC ACIDS.

(*a*) **Phthalic Acids** are the final oxidation products of all benzene derivatives in which two hydrogen atoms of the benzene nucleus have been replaced by side-chains. Hence, they are of importance in determining the position of these two side-groups in the benzene nucleus (p. 35). Their hydrogen addition products, the *hydrophthalic acids*, are also very important compounds from a theoretical standpoint. Again, o-phthalic acid is distinguished from the m- and p-bodies by its ability to form an anhydride and other cyclic derivatives. In addition to the dicarboxyl formula, the γ-dioxylactone formula has been taken into consideration for this acid. It is applied technically in the manufacture of phthaleïn dye-substances, which are of great value. The phthalic acids bear the same relation to the phthalyl alcohols, the phthalaldehydes, oxymethylbenzoic acids, and phthalaldehydic acids that oxalic acid sustains to ethylene glycol, glyoxal, glycollic acid, and glyoxalic acid:

$\begin{array}{l}CH_2OH\\ \vert\\ CH_2OH\end{array}$	$\begin{array}{l}CHO\\ \vert\\ CHO\end{array}$	$\begin{array}{l}COOH\\ \vert\\ CH_2OH\end{array}$	$\begin{array}{l}COOH\\ \vert\\ CHO\end{array}$	$\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$
Glycol	Glyoxal	Glycollic Acid	Glyoxalic Acid	Oxalic Acid
$C_6H_4\begin{cases}CH_2OH\\ CH_2OH\end{cases}$	$C_6H_4\begin{cases}CHO\\ CHO\end{cases}$	$C_6H_4\begin{cases}COOH\\ CH_2OH\end{cases}$	$C_6H_4\begin{cases}COOH\\ CHO\end{cases}$	$C_6H_4\begin{cases}COOH\\ COOH\end{cases}$
Phthalyl Alcohol	Phthalaldehyde	Oxymethyl-benzoic Acids	Phthalaldehydic Acids	Phthalic Acids.

Phthalic Acid, *Benzene-o-dicarboxylic Acid*, $C_6H_4\begin{cases}{[1]}COOH\\ {[2]}COOH\end{cases}$, $C_6H_4\begin{cases}C(OH)_2\\ CO\end{cases}\!\!>O$ (A. 269, 155), melts, when rapidly heated, at 213°, decomposing at the same time into the anhydride and water. It is obtained by oxidizing naphthalene and tetrachlornaphthalene with nitric acid. It is made technically in large amounts. It also results on oxidizing o-xylene and o-toluic acid with potassium permanganate, alizarin and purpurin with nitric acid, or with manganese dioxide and sulphuric acid; and in slight amount in the oxidation of benzene and benzoic acid. It cannot be prepared by using chromic acid as an oxidizing agent, since the latter burns it at once to carbon dioxide. It can be synthetically obtained from o-nitrobenzoic acid by converting the latter into o-cyanbenzoic acid and then boiling this with alkalies (p. 241).

History.—Laurent first obtained the acid, in 1836, by oxidizing naphthalene tetrachloride. He considered it a naphthalene derivative and named it naphthalinic acid (A. 19, 38). After Marignac had deduced the correct formula, $C_8H_6O_4$ (A. 38, 13), and demonstrated that the acid was not a derivative of naphthalene, Laurent gave it the name phthalic acid (A. 41, 107).

When heated with an excess of calcium hydroxide it yields benzene and $2CO_2$. Only $1CO_2$ is split off and calcium benzoate produced if its lime salt be heated to 330–350° with one molecule of $Ca(OH)_2$.

Sodium amalgam converts phthalic acid into di-, tetra-, and hexa-hydrophthalic acids.

Esters.—As the investigation of phthalyl chloride seemed to assign a lactone formula to this body, in which the two chlorine atoms were attached to the same carbon atom, search was made for two series of esters. However, the action of alkyl iodides upon the silver salt, and that of alcohols upon the chloride, produced the same esters (A. 238, 318).

If we disregard intramolecular atom-rearrangement, this behavior would argue for corresponding formulas for the chloride and silver salt. The *methyl ester* boils at 280°, and the *ethyl ester* at 288° (B. **16**, 860). These esters condense with acetic ester, acetone, and similar bodies in the presence of sodium ethylate, forming *diketohydrindene* derivatives. The *phenyl ester* melts at 70° (B. **7**, 705; **28**, 108). The *ethyl ester acid* is a heavy oil.

Chlorides.—The chloride of the ethyl ester-acid is a decomposable oil, produced when PCl_3 acts upon the ethyl ester-acid (B. **20**, 1011).

Phthalyl Chloride, $C_6H_4\left\{\begin{array}{l}[1]COCl\\ [2]COCl\end{array}\right.$ or $C_6H_4\left\{\begin{array}{l}[1]CO\\ [2]CCl_2\end{array}\right.>O$, solidifies at 0° and boils at 275°. It results upon heating the anhydride for several hours with an equimolecular quantity of PCl_5 at 200° (A. **238**, 329). The conversion of phthalyl chloride with glacial acetic acid and sodium amalgam into o-phthalyl alcohol is an argument favoring the sym. formula (p. 232). The unsym. formula is evident from conversion of the chloride by zinc and acetic acid into phthalide (p. 233), diphthalyl, $C_6H_4\left\{\begin{array}{l}CO>O\quad O<CO\\ C=\!=\!=\!=\!=C\end{array}\right\}C_6H_4$, and hydrodiphthalyl, and with benzene and aluminium chloride into phthalophenone or diphenylphthalide.

Phthalylene Tetrachlorides.—PCl_5 converts phthalyl chloride into **phthalylene tetrachloride**, melting at 88°, and **phthalylene tetrachloride**, melting at 47°. These cannot be changed into one another. Their crystals have been measured. Both yield phthalic acid and have been assigned the formulas $C_6H_4\left\{\begin{array}{l}CCl_3\\ COCl\end{array}\right.$ and $C_6H_4\left\{\begin{array}{l}CCl_2\\ CCl_2\end{array}\right.>O$. The formation of the two chlorides is only comprehensible from the unsymmetrical phthalyl chloride formula (B. **19**, 1188). The chloride, melting at 88°, is also obtained in the action of PCl_5 upon phthalide chloride (p. 234). This reaction argues for the unsymmetrical formula, just as well as the conversion into diphenylanthrone (see this) by condensation with benzene by means of Al_2Cl_6 or concentrated sulphuric acid (B. **28**, R. 772).

Phthalic Anhydride, $C_6H_4\left\{\begin{array}{l}[1]CO\\ [2]CO\end{array}\right.>O$, melting at 128° and boiling at 284°, sublimes readily in long needles. It results upon fusing phthalic acid or digesting it with acetyl chloride (B. **10**, 326). Phthalic anhydride yields condensation products as readily as benzaldehyde:

Thus, phthalyl acetic acid is formed on boiling the anhydride with acetic anhydride. It reacts in like manner with malonic ester and acetoacetic ester. At more elevated temperatures it combines with homologous fatty acids, with the elimination of CO_2 and the formation of alkylidene phthalides. It condenses with phthalide to diphthalyl (see this). With the phenols it yields the important phthaleïn dyes (see these), a group of triphenylmethane dyes, comprising certain beautifully fluorescent compounds. **Thiophthalic Anhydride,** $C_6H_4(CO)_2S$, melts at 114° and boils at 284° (B. **17**, 1176). **Phthalyl Superoxide,** $C_6H_4(CO_2)_2$, melts at 133°, giving gas evolution. When heated rapidly to 136° it explodes. It is formed when phthalyl chloride is acted upon with a sodium peroxide solution (B. **27**, 1511).

Phthalamic Acid, $C_6H_4\left\{\begin{array}{l}[1]COOH\\ [2]CONH_2\end{array}\right.$ or $C_6H_4\left\{\begin{array}{l}[1]C(NH_2)(OH)\\ [2]CO\text{———————}\end{array}\right.>O$, melting at 148°, is formed from the anhydride and ammonia, or when baryta-water acts upon phthalimide (B. **19**, 1402). **Anilic Acid** melts at 192°. **Phthalic Diamide,** $C_6H_4\left\{\begin{array}{l}[1]CONH_2\\ [2]CONH_2\end{array}\right.$ or $C_6H_4\left\{\begin{array}{l}[1]C(NH_2)_2\\ [2]CO\text{————}\end{array}\right.>O$, melts at 140–160°, changing at the same time to phthalimide. It is produced when ammonia acts upon the ester (B. **19**, 1399; **21**, R. 612; **24**, R. 320; **25**, R. 911).

Phthalimide, $C_6H_4\left\{\begin{array}{l}[1]CO\\ [2]CO\end{array}\right.>NH$ or $C_6H_4\left\{\begin{array}{l}[1]C(=NH)\\ [2]CO\text{———}\end{array}\right.>O$, melting at 238°, is obtained:

By heating phthalic anhydride or chloride in ammonia gas;

By heating phthalic acid with ammonium sulphocyanide (B. **19**, 2283); from phthalamide, and

By the molecular rearrangement of the isomeric o-cyanbenzoic acid (p. 236).

It forms *potassium phthalimide*, $C_6H_4(CO)_2NK$, by the action of alcoholic potash. Salts of the heavy metals can be obtained from it by double decomposition. Potassium phthalimide is readily rearranged or transposed with organic halogen derivatives, consequently it is frequently employed in the preparation of numerous amines (p. 162). While by this means alkylogens yield symmetrical alkylimides of the formula $C_6H_4(CO)_2NR$,—*e. g.*, **s-methyl- and benzylphthalimide**, melting at 132° and 115°,—unsymmetrical alkylimides of the formula $C_6H_4\left\{\begin{matrix} C:(NR) \\ CO\text{——} \end{matrix}\right\rangle O$ are obtained from the interaction of phthalalkylamic acids and acetyl chloride: unsym. *methyl-* and *benzylphthalimide* melt at 78° and 81° (B. **27**, R. 737).

Reduction changes phthalimide to phthalimidine (p. 234), while bromine and caustic potash convert it into anthranilic acid (p. 211).

Phthalanil, $C_6H_4(CO)_2NC_6H_5$, melts at 203°. It is obtained from phthalic acid and aniline; also upon boiling o benzoylbenzoic acid with aniline hydrochloride (B. **26**, 1261). **Phthalylphenylhydrazide**, $C_6H_6(CO)_2(NHNHC_6H_5)_2$, melts at 161°. *Phthalylhydrazine*, $C_6H_4(CO)_2(NH)_2$, from phthalic anhydride and hydrazine hydrate, sublimes at 200°. Phthalimide and hydrazine yield an isomeric phthalhydrazine (B. **28**, R. 429; **29**, R. 987).

a-**Phthalylphenylhydrazine**, $C_6H_4(CO)_2N.NHC_6H_5$, melts at 178°.

β-**Phthalylphenylhydrazine**, $C_6H_4\left\{\begin{matrix} CONH \\ | \\ CONC_6H_5 \end{matrix}\right.$, melts at 210° (B. **19**, R. 303; **20**, R. 255). **Phthalylhydroxamic Acid**, $C_6H_4C_2O_2NOH$, melts at 230° (B. **16**, 1781; **28**, R. 998).

Nitriles of Phthalic Acid: o **Cyanbenzoic Acid** is produced when anthranilic acid is treated with nitrous acid and cuprous cyanide. It rearranges itself, upon the application of heat, into phthalimide (B. **18**, 1496; **19**, 2283; **25**, R. 910). o-**Cyanbenzoic Acid Ester** melts at 70° (B. **19**, 1491). o-**Cyanbenzotrichloride**, $CN[2]C_6H_4CCl_3$, melting at 94° and boiling at 280°, is obtained from o-tolunitrile (B. **20**, 3199). **o-Phthalonitrile**, $C_6H_4[1,2](CN)_2$, melting at 141°, is obtained from o-amidobenzonitrile through the diazo-compound (B. **29**, 630).

Substituted o-Phthalic Acids.—Substituted naphthalenes and substituted toluic acids yield substituted phthalic acids when they are oxidized. **Tetrachlorphthalic Acid**, $C_6Cl_4(CO_2H)_2$, melts with anhydride formation at 250°. It is obtained from pentachlornaphthalene (A. **149**, 18). *Once* different ethyl esters were obtained on the one hand from the chloride, and on the other from the silver salt (A. **238**, 326); the ordinary ester melting at 60°, and another melting at 124°.

3- and 4-**Iod-o-phthalic Acids** melt at 206° and at 182° (B. **29**, 1575, R. 792). **Tetraiod-o-phthalic Acid** melts at 324–327° (B. **29**, 1634). 3- and 4-**Nitro-o-phthalic Acids** melt at 219° and 161°. 3- and 4-**Amido-o-phthalic Acids** (A. **208**, 245). **Sulpho-o-phthalic Acid** is obtained by heating naphthols, naphthylamines, and naphthalene sulphonic acids with concentrated sulphuric acid and mercury to 220–300° (B. **29**, 2806).

Oxy-o-phthalic Acids.—They are recognized by the melting points of their anhydrides, into which they change upon the application of heat.

3-Oxy-o-phthalic Acid Anhydride melts at 147° (B. **16**, 1965). **Dinitro-3-oxy-o-phthalic Acid** is *juglonic acid*, which can also be obtained by the action of nitric acid upon juglone, a naphthalene derivative (B. **19**, 168). **4-Oxy-o-phthalic Acid Anhydride** melts at 165° (A. **233**, 232).

Norhemipinic Acid-, 3,4-**Dioxyphthalic Acid Anhydride**, melting at 238°, is produced when **3,4-dichlormethoxyphthalic acid anhydride**, $(ClCH_2O)_2C_6H_2(CO)_2O$, melting at 156°,—the reaction product of PCl_5 and hemipinic acid at 180°,—is digested with water. **Hemipinic Anhydride**, 3,4-**dimethoxyphthalic anhydride**, melts at 167°. The acid is formed, together with opianic acid and meconine, in the oxidation of *narcotine;* also with meconine on fusing opianic acid with caustic potash:

$$\underset{\text{Hemipinic Acid}}{(CH_3O)_2C_6H_2\left\{\begin{matrix} COOH \\ COOH \end{matrix}\right.} \longleftarrow \underset{\text{Opianic Acid (p. 237)}}{(CH_3O)_2C_6H_2\left\{\begin{matrix} COOH \\ CHO \end{matrix}\right.} \longrightarrow \underset{\text{Meconine (p. 235).}}{(CH_3O)_2C_6H_2\left\{\begin{matrix} CO \\ CH_2 \end{matrix}\right\rangle O}$$

Consult B. **29**, R. 96, for the hemipinamido-acids and the hemipinimides.

6-Amidohemipinic Acid is produced on boiling its anhydride with baryta-water. The anhydride is **azo-opianic acid** or **2,3-dimethoxy-5,6-anthranilcarboxylic acid**, $(CH_3O)_2C_6H(CO_2H)\left\{\begin{matrix}CO\\NH\end{matrix}\right.$ (p. 238).

Normetahemipinic Anhydride melts at 247°. **Metahemipinic Anhydride** melts at 175°. **Metahemipinic Acid** or **4,5-Dimethoxy-o-phthalic Acid** was obtained in the decomposition of *papaverine* (B. **24**, R. 902). *Methylene Metahemipinic Ether Acid*, $(CH_2O_2)C_6H_2(COOH)_2$, is **hydrastic acid**, formed in the oxidation of *hydrastinine*. The oxidation of *cotarnine* yields **cotarnic acid** or *methylene methyl ether*—*3,4,5-trioxy-o-phthalic acid*, $(CH_2O_2)(CH_3O)C_6H(COOH)_2$.

Isophthalic Acid, Benzene-m-dicarboxylic Acid,

$C_6H_4\left\{\begin{matrix}[1]CO_2H\\ [3]CO_2H\end{matrix}\right.$, melts above 300° and sublimes. It is formed by oxidizing m-xylene (p. 54) and m-toluic acid with a chromic acid mixture; by the further oxidation of m-phthalyl alcohol ethyl ether, obtained from m-xylylene bromide and alcoholic potash (B. **21**, 47), and from m-dicyanbenzene and m-cyanbenzoic acid (p. 242). The last two methods permit of nucleus-syntheses from the corresponding amido-compounds, m-phenylenediamine and m-amidobenzoic acid.

The acid is also formed when potassium m-sulpho-benzoate, m-brombenzoate, and benzoate are fused with potassium formate (terephthalic acid is also formed in the last two cases); by the action of the ester of chlorcarbonic acid and sodium amalgam upon m-dibrombenzene; also by heating hydro-pyromellitic and hydro-prehnitic acids (p. 246).

Isophthalic acid is soluble in 460 parts boiling and 7800 parts cold water. It does not yield an anhydride. Reduction changes it to tetrahydroisophthalic acid. The *barium salt*, $C_6H_4(CO_2)_2Ba + 6H_2O$ (A. **260**, 30), is very soluble in water (distinction between phthalic and terephthalic acids).

The *Dimethyl-isophthalate* melts at 64°.

Isophthalyl dichloride melts at 41° and boils at 276°. The *dihydrazide* melts at 220°. Nitrous acid converts it into **isophthalazide**, $C_6H_4(CON_3)_2$, melting at 56°. Boiling alcohol converts it into m-phenylene-urethane, $C_6H_4(NHCO_2C_2H_5)_2$ (B. **29**, R. 987).

m-Cyanbenzoic Acid melts at 217° (B. **20**, 524).

m-Dicyanbenzene melts at 158° (B. **17**, 1430).

Substituted Isophthalic Acids.

The **5-chlor-**, **5-iod-**, and **5-amidophthalic acids** can be prepared from 5-nitroisophthalic acid. The nitration and sulphonation of isophthalic acid produce **5-nitroisophthalic acid** and **5-sulpho-isophthalic acid** (see benzoic acid, pp. 210, 216). The **4-brom-**, **4-iod-**, **4-amido-**, and **4-sulpho-isophthalic acids** are obtained by the oxidation of the corresponding toluic acids (B. **24**, 3778; **28**, 84; **25**, 2795; **14**, 2278). **Tetrachlor-**, **tetrabrom-**, and **tetraiod-phthalic acids** melt at 181°, 290°, and 310° (B. **29**, 1632).

Homologous Isophthalic Acids.—There are four theoretically possible methylisophthalic acids, of which *uvitic acid* may be mentioned.

Uvitic Acid, Mesidic Acid, *5-Methyl Isophthalic Acid*, $CH_3[5]C_6H_3[1,3](CO_2H)_2$, melting at 287°, is obtained by oxidizing mesitylene with dilute nitric acid. It is formed synthetically by boiling pyroracemic acid with baryta-water (p. 42). This synthesis of uvitic acid from pyroracemic acid is due to the *condensation* of two molecules of pyroracemic acid with one molecule of acetaldehyde. In this reaction a portion of the pyroracemic acid is decomposed. If a mixture of pyroracemic acid and higher fatty aldehydes be used, *homologous alkylisophthalic acids*, $C_6H_3(R)(CO_2H)_2$, will result. Thus propyl aldehyde produces *5-ethylisophthalic acid*, isobutyric aldehyde yields 5-isopropyl isophthalic acid, etc. (Doebner, B. **23**, 377). Chromic acid oxidizes these acids to

trimesic acid (p. 245); distilled with lime, uvitic acid at first yields metatoluic acid, then toluene.

Xylidic Acid, 4-*Methylisophthalic Acid*, $CH_3[4]C_6H_3[1,3](CO_2H)_2$, melting at 282°, is obtained by oxidizing pseudocumene, xylic acid, and isoxylic acid with dilute nitric acid. Potassium permanganate oxidizes it to trimellitic acid.

2-**Mesitylisophthalic Acid**, melting at 235°, results from the reduction of 2,6-dicarbonphenylglyoxylic acid with phosphorus and HI (B. **29**, R. 283).

Oxyisophthalic Acids are obtained by the same methods from oxybenzoic acids and aldehyde oxybenzoic acids as the latter are got from phenols and phenol aldehydes. Amido- and sulphocarboxylic acids also serve as starting-out material (B. **16**, 1966; **25**, R. 9).

2-**Oxy-**, 4-**Oxy-**, and 5-**Oxy-isophthalic Acids** melt at 243°, 305°, and 288°.

Oxyuvitic Acids.—Mention may be made of 4-**Oxyuvitic Acid**, $(CH_3)[5](HO)[4]$-$C_6H_2[1,3](CO_2H)_2$, produced by the action of chloroform, chloral, or trichloracetic ester upon sodium acetoacetic ester (A. **222**, 249).

Terephthalic Acid, *Benzene-p-dicarboxylic acid*, $C_6H_4[1,4](CO_2H)_2$, sublimes without melting. Isophthalic acid was obtained from m-derivatives of benzene; in a similar manner terephthalic acid is formed from p-diderivatives: p-xylene, p-toluic acid, p-dicyanbenzene, p-cyanbenzoic acid, p-dibrombenzene, etc. The best course to pursue in forming terephthalic acid is to oxidize caraway oil (a mixture of cymene and cuminol) with chromic acid, or it may be prepared from p-toluidine (B. **22**, 2178).

Terephthalic acid is almost perfectly insoluble in water, alcohol, and ether. When reduced it yields di-, tetra-, and hexahydro-terephthalic acids.

The *barium salt*, $C_8H_4O_4Ba + 4H_2O$, is very sparingly soluble in water. The *methyl ester* melts at 140°.

The *chloride* melts at 78° and boils at 259°. The *amic acid* melts at 214°. The *dihydrazide* melts above 300°. The *diazide*, $C_6H_4[1,4](CON_3)_2$, melts at 110° (B. **29**, R. 987).

p-**Cyanbenzoic Acid**, $CN[4]C_6H_4CO_2H$, from p-amidobenzoic acid (pp. 38, 214), melts at 214°.

p-**Dicyanbenzene**, $C_6H_4[1,4](CN)_2$, melts at 215°.

Mononitroterephthalic Acid melts at 259°.

It and **sulphoterephthalic** acid are produced in the nitration and sulphonation of terephthalic acid. 2,3-, 2,6-, and 2,5-**Dinitrophthalic Acids** are also known (B. **28**, 81). Consult B. **29**, 1625, 2833, for **tetrachlor-**, **tetrabrom-**, and **tetraiodterephthalic acids**.

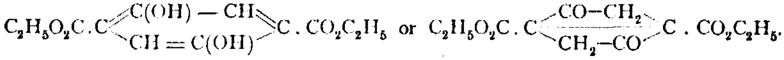
Alkyl Terephthalic Acids.—The oxidation of pseudocumene and durene gives rise to 4-**methylterephthalic acid**, *a-xylidic acid*, melting at 282°, and to 2,5-**dimethylterephthalic acid**, *β-cumidic acid* (B. **19**, 2510).

Oxyterephthalic Acids.—*Oxyterephthalic acid* has been obtained from nitroterephthalic acid. It sublimes without melting. 2,5-Dioxyterephthalic acid is the most interesting of the three possible dioxyterephthalic acids. Mention is made of it because of its connection with succino-succinic ester. Its *diethyl ester* may be prepared by withdrawing two hydrogen atoms from succino-succinic ester by means of bromine or PCl_5 (B. **22**, 2107), or by the action of sodium ethylate upon dibromacetoacetic ester (A. **219**, 78).

2,5-**Dioxyterephthalic Acid**, $(HO)_2C_6H_2(CO_2H)_2 + 2H_2O$, crystallizes from alcohol in yellow leaflets. Ferric chloride imparts a deep blue coloration to its solution. When rapidly distilled it decomposes into two molecules of carbon dioxide and hydroquinone.

2,5-**Dioxyterephthalic Ethyl Ester** crystallizes in two distinct forms: at the ordinary temperature in *yellowish-green prisms* or plates; at higher temperatures in *colorless leaflets*. It also sublimes in the latter form. It melts at 133°. In most of its reactions the ester conducts itself like an hydroxyl derivative. It does not combine with hydroxylamine or

phenylhydrazine, and with sodium and alkyl iodides yields dialkyl esters.* It, however, does not react with phenylcyanate (p. 89) (B. 23, 259), and shows some analogies with succino-succinic ester. Hence, it is considered a quinone- or diketo-derivative.



Dioxyterephthalic ester, by reduction (boiling with zinc and hydrochloric acid in alcoholic solution), is again changed to succino succinic ester (B. 19, 432; 22, 2169). A dihydroxamic acid is formed with hydroxylamine hydrochloride; **tetrahydrodioxyterephthalic acid** is produced at the same time (B. 22, 1280). The different physical modifications of the ester and analogous compounds, according to Hantzsch, correspond to two desmotropic conditions—the colored variety agreeing with the quinone formula, while the colorless corresponds to the hydroxyl formula (B. 22, 1294). However, the color cannot be regarded as a certain criterion for the distinction of the ketone from the hydroxyl form. Even chemical reactions do not prove that desmotropic forms can be accepted (Nef, B. 23, R. 585; Goldschmidt, B. 23, R. 260).

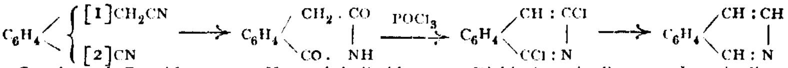
Succino-succinic Acid, whose ester by the removal of hydrogen yields 2,5-dioxy terephthalic ester, will be discussed in connection with the hydro aromatic compounds.

Trioxydicarboxylic Acids.—**Gallocarboxylic Acid**, *Trioxy o-phthalic Acid*, $(HO)_3$-$[3,4,5]C_6H(CO_2H)_2$, melts at 270°, with decomposition. It may be prepared from pyrogallol by heating it to 130° with ammonium carbonate. Pyrogallo-carboxylic acid is formed at the same time (B. 13, 1876).

(*b*) **Aromatic Dicarboxylic Acids** *containing* $1CO_2H$ *in the nucleus and* $1CO_2H$ *in the side-chain.* The three *a*-homophthalic acids, or phenylacetic carboxylic acids, are known. The o-acid readily forms heterocyclic derivatives.

Phenylaceto-o-carboxylic Acid, o-*a-homophthalic acid*, $CO_2H[2]C_6H_4CH_2 . CO_2H$, melting at 175°, with the elimination of water, may be obtained by fusing gamboge with caustic potash (B. 19, 1654), and by saponifying cyan-o-toluic acid. Its *anhydride* melts at 141°.

o-**Homophthalimide,** melting at 233°, is produced when the ammonium salt is heated, and when acids act upon the dinitrile. In the latter case o cyanphenylacetic acid, produced at first, rearranges itself into homophthalimide, just as o-cyanbenzoic acid yields phthalimide (p. 240) (B. 23, 2478). It is rather remarkable that o-homophthalimide, when heated with phosphorus oxychloride, yields *dichlorisoquinoline*, which becomes *isoquinoline* when further heated with hydriodic acid (B. 27, 2232, 2492):



o-Cyanbenzyl Cyanide Homophthalimide Dichlorisoquinoline Isoquinoline.

Homophthalimide is directly converted into isoquinoline when it is heated with zinc-dust.

The hydrogen atoms of the CH_2-groups are replaced by two alkyls when homophthalimide is heated with caustic potash and alkyl iodides. *Mono*-alkyl-o-benzylcyanides yield monoalkyl homophthalimides, which rearrange themselves in the same manner as homophthalimide into *alkyl isoquinolines* (B. 20, 2499).

ω-Cyan-o-toluic Acid, $CO_2H[2]C_6H_4CH_2CN$, melts with decomposition at 116°. Its potassium salt is obtained from phthalide (p. 234) and potassium cyanide (A. 233, 102).

o **Cyanbenzyl Cyanide,** o-*a-Homophthalonitrile*, $CN[2]C_6H_4CH_2CN$, melting at 81°, is obtained from o-cyanbenzyl chloride (p. 234). Caustic potash and alkylogens effect the replacement of an hydrogen atom in the methylene group by an alcohol radical (see homophthalimide). Acetyl chloride converts it into **ψ-diacetyl-o-cyanbenzyl cyanide,** $CN . C_6H_4C(CN) : C(CH_3)OCOCH_3$, which may be rearranged into 3-methylisoquinoline (B. 27, 2232).

Homoisophthalic Acid and **homoterephthalic acid** melt at 237°. Both sublime. m and p-**Cyanbenzyl Cyanides** melt at 88° and 100° (B. 24, 2416). The *dinitrile*,

the two *nitrilo*- and *amic* acids, the two possible *amido-nitriles*, and the *diamide* of homoterephthalic acid have been prepared (B. **22**, 3207; **26**, R. 89, 602).

o-**Hydrocinnamic Carboxylic Acid**, $CO_2H[2]C_6H_4CH_2CH_2CO_2H$, melts at 165°. It is formed by oxidizing *tetrahydro-β-naphthylamine* with potassium permanganate, and by the reduction of dihydroisocoumarine carboxylic acid (B. **26**, 1841), as well as from o-carbonphenyl glyceric acid-δ-lactone (B. **25**, 888). It yields α-hydrindone (B. **26**, 708) upon dry distillation.

o-**Cyanbenzyl Acetic Ester, Cyanhydrocinnamic Ester**, $CN[2]C_6H_4[1]\cdot CH_2\,CH_2.CO_2C_2H_5$, melting at 98°, is produced by the rearrangement of the product resulting from the action of acetoacetic ester or malonic ester and sodium ethylate upon cyanbenzyl chloride (B. **22**, 2017). Concentrated hydrochloric acid converts it into α-hydrindone (see this): $C_6H_4<{CH_2 \atop CO}>CH_2$.

Phenylbutyric-o-carboxylic Acid, $CO_2H[2]C_6H_4CH_2.CH_2.CH_2.CO_2H$, melts at 138° (B. **18**, 3118).

(*c*) **Aromatic Dicarboxylic Acids**, having both carboxyls in different side-groups.

o-, m-, and p-**Phenylene Diacetic Acids**, $C_6H_4(CH_2CO_2H)_2$, melting at 150°, 170°, and 244°, have been obtained from the xylylene cyanides (B. **26**, R. 941). o-Phenylene diacetic acid has also been prepared by oxidizing dihydronaphthalene (see this). Its calcium salt yields β-hydrindone upon distillation (see this) (B. **26**, 1833).

o-**Phenyleneaceto-propionic Acid**, $C_6H_4(CH_2.COOH)[2](CH_2.CH_2COOH)$, melting at 139°, is obtained from β-oxy-α-naphthoic acid by rupture of the ring, effected by sodium and amyl alcohol, just as pimelic acid is formed from salicylic acid (pp. 47, 222). It reverts to β-ketotetrahydronaphthalene when its calcium salt is distilled (B. **28**, R. 745).

o-, m-, and p-**Phenylene Dipropionic Acids**, $C_6H_4(CH_2.CH_2.CO_2H)_2$, melting at 161°, 146°, and 223°, are formed from xylylene dimalonic acids (B. **19**, 436; **21**, 37).

9. ALDEHYDO-DICARBOXYLIC ACIDS.

2-**Aldehydo-isophthalic Acid**, melting at 175° to 176°, results from heating 2,6-dicarbophenylglyoxylic acid (B. **26**, 1797; **30**, 695).

5-**Aldehydo-4-oxy- and 5-aldehydo-3-oxyisophthalic acids** are formed from the corresponding oxyisophthalic acids by means of chloroform and caustic potash (B. **11**, 793).

10. TRICARBOXYLIC ACIDS.

The three isomeric benzene tricarboxylic acids, $C_6H_3(CO_2H)_3$, are known. **Trimesic Acid**, (1,3,5)-*Benzenetricarboxylic Acid*, melts about 300°, and sublimes near 200°. It is formed (1) when mesitylenic and uvitic acids are oxidized with a chromic acid mixture; (2) by heating mellitic acid with glycerol, or hydro- and isohydromellitic acid with sulphuric acid. A synthetic method for its production consists in (3) heating benzene-1,3,5-trisulphonic acid with potassium cyanide and saponifying the resulting cyanide. By the condensation of certain aliphatic substances the acid and its esters have been obtained (1) by polymerizing propiolic acid; (2) by the production of its monomethyl ester through the action of caustic potash upon coumalic acid (B. **24**, R. 750); (3) its triethyl ester from formyl acetic ester. Its **trimethyl ester** melts at 143°. Its **triethyl ester** melts at 133°.

Trimellitic Acid, (1,2,4)-*Benzene tricarboxylic Acid*. This is obtained (together with isophthalic acid) by heating hydropyro-mellitic acid with sulphuric acid, or upon oxidizing xylidic acid with potassium permanganate, also from amidoterephthalic acid (B. **19**, 1635). It is prepared most readily (along with isophthalic acid) by oxidizing colophony with nitric acid (A. **172**, 97). It melts at 216°, decomposing into water and the anhydride, $C_6H_2(CO_2H)(CO)_2O$. The latter melts at 158°.

Hemimellitic Acid, (1,2,3)-*Benzene tricarboxylic Acid*. This is formed on heating hydromellophanic acid (below) with sulphuric acid, as well as in the oxidation of phenyl-

glyoxyldicarboxylic acid, formed from naphthalic acid by action of $KMnO_4$ (B. **29**, 283). It melts at 185° and decomposes into phthalic anhydride.

Oxytricarboxylic Acids have been obtained from the sulphotricarboxylic acids: **oxytrimesic acid** (A. **206**, 204); **oxytrimellitic acid**—see B. **16**, 192.

Phloroglucin-tricarboxylic ester and **dioxyphenylaceto-dicarboxylic ester**, condensation products of sodium malonic ester and sodium acetone dicarboxylic ester, are probably hydroaromatic compounds.

11. AROMATIC TETRACARBOXYLIC ACIDS.

The three isomerides are known. Reduction converts them into tetrahydrobenzene tetracarboxylic acids (see these).

Pyromellitic Acid, 1,2,4,5-*Benzene Tetracarboxylic Acid*, $C_6H_2(CO_2H)_4 + 2H_2O$, melts when anhydrous at 264° and decomposes into water and its anhydride, which is produced when mellitic acid is distilled, or, better, when the sodium salt is subjected to the same treatment with sulphuric acid. The acid is also produced by oxidizing durene and durylic acid with potassium permanganate.

The *dianhydride*, $C_6H_2\left(\begin{matrix}CO\\CO\end{matrix}>O\right)_2$, melts at 286°. The *ethyl ester*, $C_6H_2(CO_2 . C_2H_5)_4$, melts at 53°.

Dinitro- and **diamidohydromellitic tetraethyl esters** melt at 130° and 134°. Nitric acid oxidizes the diamido-ether to:

Quinone Tetracarboxylic Ester, $C_6(O_2)(CO_2 . C_2H_5)_4$, crystallizing in quinone-yellow needles, melting at 149°. It is odorless, but sublimes quite readily. Zinc reduces it in glacial acetic acid solution to—

Hydroquinone Tetracarboxylic Ester, $C_6(OH)_2(CO_2 . C_2H_5)_4$, crystallizing in bright yellow needles, melting at 127°. In alcoholic solution it is reduced by zinc-dust and hydrochloric acid to p-diketohexamethylene tetracarboxylic ester (A. **237**, 25).

Prehnitic Acid, (1,2,3,4) *benzene tetracarboxylic acid*, $C_6H_2(CO_2H)_4 + 2H_2O$, melts when anhydrous at 237°, with the formation of an anhydride. It results (together with mellophanic acid and trimesic acid) upon heating hydro- and isohydro-mellitic acid with sulphuric acid, also by oxidizing prehnitol with potassium permanganate (B. **21**, 907).

Mellophanic Acid (1,2,3,5)-*benzene tetracarboxylic acid*, melts at 238°, with anhydride formation. It is formed by the oxidation of isodurene with $KMnO_4$; see prehnitic acid.

12. AROMATIC PENTACARBOXYLIC ACID.

Benzene Pentacarboxylic Acid, $C_6H(CO_2H)_5 + 6H_2O$, decomposes when it is melted. It is produced by oxidizing penta-methylbenzene with permanganate (B. **17**, R. 376).

13. AROMATIC HEXACARBOXYLIC ACID.

Mellitic Acid, $C_6(CO_2H)_6$. When heated it melts and decomposes into water, carbon dioxide, and pyromellitic anhydride.

Honey-stone, found in some lignite beds, is an aluminium salt of mellitic acid, crystallizing in large quadratic pyramids of bright yellow color (B. **10**, 566).

An interesting formation of mellitic acid is that whereby pure carbon (graphite, charcoal, etc.) is oxidized with an alkaline solution of potassium permanganate. Another is when the carbon is applied as positive electrode in electrolysis (B. **16**, 1209), and also the oxidation of hexamethyl benzene with $KMnO_4$.

As hexamethyl benzene can be synthesized, this latter method of formation would be a synthesis of mellitic acid.

Mellitic acid crystallizes in fine, silky needles, readily soluble in water and alcohol. It is very stable, and is not decomposed by acids, by chlorine, or bromine, even upon boiling. It yields benzene when distilled with lime.

History.—Klaproth (1799) discovered mellitic acid by boiling honey-stone for a long period with water, and named it honey-stone acid. In 1870 Baeyer proved that mellitic acid was nothing more than benzene hexacarboxylic acid, in that by heating with lime he obtained benzene and by reduction found hexahydromellitic acid (A. suppl., 7, 1).

Salts and Esters.—The *barium salt*, $C_{12}Ba_3O_{12} + 3H_2O$, is insoluble in water. The *methyl ester* melts at 187°; the *ethyl ester* melts at 73°.

The **chloride**, $C_6(COCl)_6$, melts at 190°.

Mellimide, Paramide, $C_6\left(\begin{matrix}CO\\CO\end{matrix}>NH\right)_3$, is formed in the dry distillation of the ammonium salt. It is a white, amorphous powder, insoluble in water and alcohol. Heated to 200° with water, it is converted into the tri-ammonium salt of mellitic acid. The alkalies convert paramide into euchroic acid.

Euchroic Acid, $C_6[(CO)_2NH]_2\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$, crystallizes in colorless prisms. Heated with water to 200°, it yields mellitic acid. Nascent hydrogen changes euchroic acid to *euchrone*, a dark blue precipitate, which reverts to colorless euchroic acid upon exposure. Euchrone dissolves with a dark red color in alkalies.

3. AROMATIC POLYALCOHOLS, CONTAINING MORE THAN ONE HYDROXYL GROUP IN THE SAME SIDE-CHAIN, AND THEIR OXIDATION PRODUCTS.

Of the aromatic polyalcohols, having the hydroxyl groups attached to different carbon atoms of the same side-chain, it is only the glycols and their oxidation products which have been studied in any sense completely. A more detailed classification of the polyhydric alcohols and their oxidation products is therefore unnecessary; the compounds belonging here will, for practical considerations, be included with the glycols and their oxidation products.

The methods of formation as they were applied in the preparation of aliphatic glycols and their oxidation products (1, 289) are more extensively and fully used for the phenyl glycols and their oxidation products than they have been in connection with any of the previously discussed aromatic derivatives.

1. PHENYL GLYCOLS AND PHENYL GLYCEROL.

Styrolene Alcohol, $C_6H_5.CH(OH).CH_2.OH$, *Phenyl glycol*, melts at 67°, boils at 273°, and is obtained from styrolene dibromide by the action of a potash solution. Dilute nitric acid oxidizes it to benzoyl carbinol and benzoyl formic acid (A. **216**, 293). Two molecules are condensed by dilute sulphuric acid to β-phenyl naphthalene (see this). **Styrolene Dichloride**, *a,β-dichlorethyl benzene*, $C_6H_5CHCl.CH_2Cl$, is liquid, while the **dibromide** melts at 60°. They result from the addition of halogens to styrene (see this) or phenylethylene.

Phenyl Methyl Glycol, $C_6H_5.CH(OH).CH(OH).CH_3$, exists in two modifica-

tions, α and β, like hydrobenzoïn. These are obtained from phenyl dibrompropane (from n-propyl benzene). The α-body melts at 53°, the β- at 93° (B. **17**, 709).

Phenyl Butylene Glycol, $C_6H_5CH(OH)CH_2 . CH_2 . CH_2(OH)$, melting at 75°, is obtained by reduction from benzoylpropionic aldehyde (p. 250) and benzoylpropyl alcohol.

Phenylisopropyl Ethylene Glycol, $C_6H_5CH(OH)CH(OH)CH(CH_3)_2$, melting at 81° and boiling at 286°, results from the reduction of benzaldehyde and isobutylaldehyde.

Methylene-m,p-dioxybenzyl Glycol, $[CH_2O_2][3,4]C_6H_3CH_2CH(OH)CH_2(OH)$, melting at 82°, and **Methylene-m,p-dioxyphenylethylenemethyl Glycol**, (CH_2O_2)-$[3,4]C_6H_3 . CH(OH) . CH(OH) . CH_3$, melting at 101°, result from the action of $KMnO_4$ (B. **24**, 3488) upon *safrol* and *isosafrol*. The corresponding glycols, melting at 68° and 88°, are obtained from *eugenol* and *isoeugenol* (see these).

Stycerine, $C_6H_5 . CH(OH) . CH(OH) . CH_2 . OH$, a gummy mass, is obtained from styrone bromide and cinnamic alcohol, $C_6H_5 . CHBr . CHBr . CH_2 . OH$, with potassium permanganate (B. **24**, 3491).

2. PHENYLALCOHOL ALDEHYDES.

Just as two molecules of acetaldehyde condense to aldol, so the nitrobenzaldehydes combine with acetaldehyde, under the influence of very dilute sodium hydroxide (2 per cent.) to the corresponding aldols, the **nitrophenyl-lactic acid aldehydes**, $NO_2C_6H_4$-$CH(OH)CH_2CHO$, which unite with an additional molecule of acetaldehyde. Dehydrating agents, like acetic anhydride, convert them into the corresponding nitrocinnamic aldehydes (B. **18**, 719).

Phenyltetrose, $C_6H_5 . CH(OH)CH . OH . CH(OH) . COH$, is a colorless syrup resulting from the reduction of phenyltrioxybutyric acid lactone (see this). Its *phenylhydrazone* melts at 154°.

3. PHENYL KETOLS.

Acetophenone Alcohol, *Benzoyl Carbinol*, $C_6H_5 . CO . CH_2 . OH$, crystallizes from water and dilute alcohol in large, brilliant leaflets, which contain water of crystallization, and melt at 73–74°. It crystallizes from ether in shining anhydrous plates, and melts at 85°. It is produced in the oxidation of phenyl glycol, and from its chloride, ω-chloracetophenone, by its conversion into acetate and saponification with potassium carbonate (B. **16**, 1290).

When distilled it decomposes, with formation of bitter-almond oil. Being a ketone, it forms crystalline compounds with primary alkaline sulphites. Like acetyl carbinol, it reduces a cold ammoniacal silver or copper solution (forming benzaldehyde and benzoic acid), and is oxidized to mandelic acid (p. 251) (B. **14**, 2100). Nitric acid oxidizes it to phenylglyoxylic acid. It yields cyanhydrin with CNH, which then forms α-phenylglyceric acid, or atroglyceric acid (see this).

Bismethylbenzoyl Carbinol,
$$\begin{array}{l} C_6H_5C(O . CH_3)—O—CH_2 \\ \quad | \qquad\qquad\qquad\qquad\quad | \\ \quad CH_2————O—C(OCH_3)C_6H_5 \end{array}$$
(?), melting at 192°, is formed from benzoyl carbinol with methyl alcohol and hydrochloric acid (B. **28**, 1161).

Benzoyl Carbinol Acetate, $C_6H_5CO . CH_2 . O . COCH_3$, melts at 49° and boils at 270°. The *benzoate* melts at 117°. The *phenyl-ether* melts at 72°.

ω-**Chloracetophenone**, *Phenacyl Chloride*, *Benzoyl Carbinol Chloride*, C_6H_5CO-CH_2Cl, melting at 59° and boiling at 245°, results from the chlorination of boiling acetophenone (B. **10**, 1830), as well as from benzene, chloracetyl chloride, and aluminium chloride.

ω-**Bromacetophenone**, $C_6H_5 . CO . CH_2Br$, melting at 50°, attacks the mucous membrane quite powerfully. It is obtained from acetophenone and bromine, also by heating dibromatrolactinic acid with water (B. **14**, 1238). An excess of alcoholic ammonia changes it to *isoindol*—a hydrazine derivative. The acid amides and thiamides change the ω-haloid acetophenones into *oxazole* and *thiazole* derivatives (see these).

Gallo-chlor-acetophenone, $C_6H_2(OH)_3COCH_2Cl$, and **ω-bromresacetophenone**, containing the hydroxyl group in the ortho-position, part with halogen hydrides, and become *ketocumaran-* or *ketodihydrocumarone* derivatives (B. **30**, 299).

ω-Amidoacetophenone, $C_6H_5.CO.CH_2.NH_2$, is very unstable in a free condition. Separated from its hydrochloride by means of sodium hydroxide, it changes to the base $C_{16}H_{14}N_2O$, melting at 118°, which yields *isoindol* in the presence of ammonia. The *hydrochloride*, $C_6H_5.CO.CH_2.NH_2HCl$, melting at 183°, is formed when the isonitrosoacetophenone is reduced with tin and hydrochloric acid (B. **28**, 254). For the action of nitrous acid upon the hydrochloride see B. **26**, 1717; **29**, R. 298. Potassium cyanate (B. **28**, 252) produces phenylacetylene monoureïn, or phenylimidazolon (see this). **ω-Acetophenone-anilide**, *phenacyl anilide*, $C_6H_5.CO.CH_2.NHC_6H_5$, melting at 93°, is formed from ω-bromacetophenone and aniline (B. **15**, 2467), and may be condensed to α-phenylindol (B. **21**, 1071, 2196, 2595).

Benzoylcarbinoloxime melts at 70°. The *phenylhydrazone*, melting at 112°, is converted by phenylhydrazine into an osazone of phenylglyoxal (B. **20**, 822).

o- and m-**Nitro-ω-bromacetophenones** melt at 55° and 96° (A. **221**, 327).

α-Amidopropiophenone, $C_6H_5.CO.CHNH_2.CH_3$ (B. **22**, 3250).

Corresponding to the nitrophenyllactic acid aldehydes we have o- and p-**Nitrophenyllactic acid ketones**, melting at 69° and 58°; these are the condensation products of o- and p-nitrobenzaldehyde and acetone in the presence of very dilute sodium hydroxide. Boiling water or an excess of sodium hydrate causes the o-nitroketone to give up acetic acid and water, changing thereby into *indigo* (B. **16**, 1968). See the nitrobenzylidene acetones.

Benzoylbutylcarbinol, $C_6H_5.CO.[CH_2]_3.CH_2OH$, melts at 40° (B. **23**, R. 500).

4. PHENYLALDEHYDE KETONES.

α-Ketone Aldehydes.—**Phenyl Glyoxal**, *Benzoyl formaldehyde*, $C_6H_5.CO.CH(OH)_2$, melts at 73°. The anhydrous aldehyde boils at 142° (125 mm.). It has a penetrating odor. It is obtained from its aldoxime, isonitrosoacetophenone, upon boiling the sodium sulphite derivative with dilute sulphuric acid (B. **22**, 2557). Alkalies convert it into mandelic acid (p. 251); potassium cyanide condenses it to benzoylformoïn, just as it changes benzaldehyde to benzoïn. It yields quinoxalines with o-diamines.

ω-Dichloracetophenone, $C_6H_5.CO.CHCl_2$, boils at 253° (B. **10**, 531). **ω-Dibromacetophenone**, $C_6H_5.CO.CHBr_2$, melts at 36° (B. **10**, 2010; A. **195**, 161). **ω-Dibrom-p-iodacetophenone** (B. **24**, 997). **ω-Dichlor-o-nitroacetophenone** melts at 73° (A. **221**, 328). **ω-Dibrom-o-, -m-, and p-nitroacetophenones** melt at 85°, 59°, and 98° (B. **20**, 2203; **18**, 2240; **22**, 204).

Isonitrosoacetophenone, *Benzoylformoxime*, $C_6H_5CO.CH(N.OH)$, melting at 127°, is obtained from acetophenone (p. 189) (B. **24**, 1382; **25**, 3459). It forms isoindol (p. 248) by reduction. **Phenyl Glyoxime**, $C_6H_5C(NOH).CH(NOH)$, is known in two modifications (compare benzildioximes):

$$\begin{array}{ccc} C_6H_5.C\!-\!\!-\!\!-\!C.H & & C_6H_5C\!-\!CH \\ \quad\ \| \qquad\ \| \quad (?) & & \ \| \quad \| \quad (?) \\ N.OH \ \ N.OH & & HO.N \ \ N.OH \end{array}$$

Phenylamphiglyoxime (melts at 168°) — Phenylantiglyoxime (melts at 180°).

Phenylamphiglyoxime is produced when hydroxylamine acts upon ω-dibromacetophenone and isonitrosoacetophenone. When treated in absolute ether with hydrochloric acid gas, it changes to the anti-modification, which reverts to the amphi-modification by recrystallization from indifferent solvents (B. **24**, 3497).

α- and β-**Phenylglyoxalphenylhydrazones** melt at 142° and 129° (B. **22**, 2557).

Phenylglyoxalphenylosazone, $C_6H_5.C:(N.NH.C_6H_5).CH:(N.NHC_6H_5)$, melts at 152°. (See benzoylcarbinolphenylhydrazone) (B. **22**, 2558). **Phenylglyoxalmethylphenylosazone** melts at 152° (B. **21**, 2597).

p-Toluic formaldehyde, $CH_3C_6H_4CO.CH(OH)_2$, melts at 101° (B. 22, 2560).

Anthroxanaldehyde, $C_6H_4\left\{\begin{array}{l}[1]\,C\text{—}CHO \\ [2]\,N{>}O\end{array}\right.$, melting at 72°, is formed from o-nitrophenylglycidic acid (p. 256) (B. **16**, 2222) (compare anthranil, p. 212).

β-Keton-aldehydes.—Formylacetophenone, or *benzoylacetaldehyde*, was formerly regarded as β-keton-aldehyde, in which, as in formylacetone, an unsaturated ketol, oxymethylene-acetophenone, is present. This will, therefore, be discussed later in connection with the compounds containing an unsaturated side chain. The sodium salt of oxymethylene-acetophenone and hydroxylamine hydrochloride yield **benzoylacetaldoxime**, $C_6H_5.CO.CH_2.CH:N.OH$, melting at 86°, which acetic anhydride converts into cyanacetophenone (p. 260), and acetyl chloride into the isomeric phenylisoxazole.

γ-Keton-aldehydes.—**Benzoylpropionaldehyde**, $C_6H_5CO.CH_2.CH_2.CHO$, boils at 245°.

5. PHENYL PARAFFIN DIKETONES.

α-Diketones, or *orthodiketones*, are produced from their monoximes, the phenylisonitrosoketones (compare phenylglyoxal) by distillation with dilute acids (1, 326), or by digesting with amyl nitrite (B. **21**, 2177). **Benzoyl Acetyl**, $C_6H_5.CO.CO.CH_3$, boiling at 214°, is a yellow oil with a peculiar odor (B. **21**, 2119, 2176).

α-**Oximidopropiophenone**, $C_6H_5.CO.C:(NOH).CH_3$, melting at 113°, results from the action of nitrous acid upon methylbenzoylacetic ester.

Di-isonitrosoanethol Peroxide, $\begin{array}{c}NO\text{—}ON \\ \| \quad\quad \| \\ CH_3O[4]C_6H_4.C\text{——}C.CH_3\end{array}$, melting at 97°, results from the action of sodium nitrite upon anethol in glacial acetic acid solution (B. **26**, R. 891).

The β- or *meta-diketones* result, together with acetophenone, (1) from the decomposition of the benzoylacetoacetic esters (B. **16**, 2239); further, by (2) a remarkable condensation induced by sodium alcoholate (Claisen, B. **20**, 2178).

The β-diketones behave like the β-diketones of the fatty series. They dissolve in alkalies. This distinguishes them from the other diketones. They are colored an intense red by ferric chloride. They condense to *isoxazoles* with hydroxylamine (B. **21**, 1150). They form pyrazole compounds with phenylhydrazine, just like the oxymethylene-β-ketones.

Benzoyl Acetone, *acetyl acetophenone*, $C_6H_5.CO.CH_2.CO.CH_3$, melts at 60–61°, boils at 260–262°, and readily volatilizes with steam. It is formed from benzoylacetoacetic ester, from ethyl benzoate and acetone or ethyl acetate and acetophenone with sodium ethylate, free from alcohol. See B. **27**, 1571, for the addition of CNH to benzoyl acetone. See J. pr. Ch. [2] **48**, 489, for the action of urea and guanidine. o-**Nitrobenzoyl Acetone** melts at 55° (A. **221**, 332).

Propionyl-, butyryl-, isobutyryl-, and **valerylacetophenones** boil at 172° (30 mm.), 174° (24 mm.), 170° (26 mm.), and 183° (30 mm.) (B. **20**, 2181).

Phenyl-acetyl-acetone, $C_{11}H_{12}O_2 = C_6H_5.CH_2.CO.CH_2.CO.CH_3$, boiling at 266°, results from the decomposition of phenyl acetyl-acetoacetic ester (B. **18**, 2137).

The following is a γ-diketone:

Acetophenone-acetone, *phenacylacetone*, $C_6H_5.CO.CH_2.CH_2.CO.CH_3$, is obtained from acetophenone acetoacetic ester. It is a yellow oil, boiling with decomposition (B. **17**, 2756).

Being a γ-diketone, it can split off water and yield phenylmethylfurfurane, phenylmethylthiophene, and phenylmethyl pyrrol.

Triketones.—**Isonitrosobenzoyl Acetone**, $C_6H_5CO.C(NOH).CO.CH_3$, melting at 24°, is the monoxime of a triketone (B. **17**, 815).

6. PHENYL PARAFFIN ALCOHOL ACIDS.

A. **Monoxyalcohol Acids.**—Phenylalcohol carboxylic acids, like the aliphatic alcohol acids, are produced (1) by the reduction of the corresponding ketonic acids; (2) from aldehydes and ketones (B. **12**,

815) by the addition of hydrocyanic acid and the saponification of the α-oxy-acid nitrile; (3) from the corresponding monohalogen acids; (4) from unsaturated monocarboxylic acids, etc.

α-and β-**Oxy-acids.—Mandelic Acid, Phenylglycollic Acid,** $C_6H_5.\overset{*}{C}HOH.CO_2H$, is isomeric with the cresotinic acids (p. 225) and the oxymethylbenzoic acids (p. 234) or carbinol benzoic acids. It contains an asymmetric carbon atom, and therefore, like lactic acid of fermentation (1, 335), appears in one inactive, decomposable and two optically active modifications.

Paramandelic Acid, *inactive mandelic acid,* melting at 118°, is formed (1) from benzaldehyde, prussic acid, and hydrochloric acid (B. **14**, 239, 1965); (2) from benzoylformic acid (p. 257), by reduction with sodium amalgam; and (3) from phenylchloracetic acid by boiling it with alkalies (B. **14**, 239), (4) as well as from ω-dibromacetophenone (p. 249) or phenyl glyoxal (p. 249) by the action of alkalies: $C_6H_5.CO.CHO \longrightarrow C_6H_5.CHOH.CO_2H$.

The production of alcohol and carboxylic acid, which completes itself extramolecularly in the action of caustic alkali upon benzaldehyde, in the case of the conversion of phenyl glyoxal into mandelic acid proceeds intramolecularly (1, 321). See further on for the formation of paramandelic acid from lævo- and dextromandelic acids.

One hundred parts water at 20° dissolve 15.9 parts of paramandelic acid. Dilute nitric acid converts it first into benzoyl-formic acid, then into benzoic acid. When heated with hydriodic acid it forms phenyl-acetic acid; with hydrobromic and hydrochloric acids, chlorphenyl or bromphenyl acetic acids.

Lævo- and dextromandelic Acids melt at 133°. They have equal, but opposite, molecular rotatory power. Toward reagents they behave like paramandelic acid. Lævomandelic acid, *natural mandelic acid,* results upon digesting amygdalin (see this) with fuming hydrochloric acid (1848—Wöhler, A. **66**, 240). Fermentation of ammonium paramandelate with *Penicillium glaucum* destroys the lævo- and there remains the dextro-acid. Schizomycetes first destroys the dextro-mandelic acid in paramandelic acid; the lævo-acid remains (Lewkowitsch, B. **17**, 2723). The direct splitting up of paramandelic acid into the dextro- and lævo-acids can be brought about by the crystallization of the cinchonine salt. The mixing together of the dextro- and lævo-acids (molecular quantities) results in the formation of inactive paramandelic acid. When the dextro- or lævo-acid is heated in a tube to 160°, it is converted into the inactive mandelic acid.

Derivatives of Paramandelic Acid.—The *methyl* and *ethyl esters* melt at 52° and 34° (B. **28**, 259). The *methyl ether-acid* melts at 71°. The *dimethyl ether-acid* boils at 246° (A. **220**, 40). *Acetyl Ethyl Ester* melts at 74°. *Mandelic Chloralide* (1, 340) melts at 82° (A. **193**, 40). The *amide* melts at 131° (B. **25**, 2212).

Mandelic Acid Nitrile, $C_6H_5.CHOH.CN$, is a colorless oil, solidifying at —10°. At 170° it breaks down into prussic acid and benzaldehyde. On standing with fuming hydrochloric acid it passes into the amide; and, when heated, into phenylchloracetic acid (B. **14**, 1967). It condenses with benzaldehyde to *diphenyloxazole* (B. **29**, 207; R. 791).

p-**Brom-** and p-**iod-mandelic acids** melt at 117° and 133° (B. **24**, 997; **23**, 3467). o-, m-, and p-**Nitromandelic Acids** melt at 140°, 119°, and 126° (B. **20**, 2203; **22**, 208).

o-**Amido-mandelic Acid,** *Hydrindic Acid,* $NH_2[2]C_6H_4CH(OH)CO_2H$, is not stable in a free condition. Its sodium salt, $C_8H_8NO_3Na + H_2O$, is formed in the reduction of isatin with sodium amalgam. From concentrated solutions of the sodium salt acids separate

Dioxindol, *o-Amidomandelic acid lactam,* $C_6H_4\left\{\begin{matrix}[1]CH(OH)CO \\ [2]NH\text{———}\rfloor\end{matrix}\right.$. This is also produced when isatin and zinc-dust, water, and some hydrochloric acid are boiled.

Acetyldioxindol, melting at 127°, is converted by baryta-water into o-**acetamidomandelic acid**, $CH_3CONH[2]C_6H_4CH(OH)CO_2H$, melting at 142°, which also results from the reduction of acetylisatinic acid. Hydriodic acid or sodium amalgam changes it to oxindol (p. 224).

p-**Dimethylamidophenyl-trichlorethyl alcohol** (p. 187) is a derivative of p-amidomandelic acid.

o-**Oxymandelic Acid**, obtained from salicylaldehyde, prussic acid, and also from o-oxyphenyl glyoxylic acid, is a syrupy mass. Its *lactone* melts at 49° and boils at 237° (B. 14, 1317; 17, 974). p-**Methoxymandelic Acid**, from anisaldehyde, melts at 93° (B. 14, 1976).

Phenylchloracetic Acid, $C_6H_5.CHCl.CO_2H$, melting at 78°, is produced when mandelic acid is heated with concentrated hydrochloric acid to 140°, and by action of water upon its chloride. Its *chloride*, $C_6H_5.CHCl.COCl$, formed by the action of PCl_5 upon mandelic acid, boils at 125° (45 mm.) (A. 279, 122).

Phenylbromacetic Acid, $C_6H_5.CHBrCO_2H$, melts at 83°. Its *ethyl ester*, boiling at 145° (10 mm.) (B. 24, 1877), when heated with potassium cyanide becomes diphenylsuccinic ester. Its *nitrile*, from benzyl cyanide and bromine, when heated alone becomes stilbene; when heated with potassium cyanide it yields stilbene or dicyandibenzyl (see this); while with alcoholic potash, stilbene dicarboxylic acid or diphenyl maleïc acid is produced.

Phenylamido-acetic Acid, $C_6H_5.CH(NH_2).CO_2H$, melts at 256°. It yields CO_2 and benzylamine when it is distilled. It results (1) on treating phenylbromacetic acid with aqueous ammonia (B. 11, 2002); (2) on boiling its nitrile with dilute sulphuric acid (B. 13, 383), and (3) by the reduction of its oxime or the phenylhydrazone of benzoyl formic acid (A. 227, 344). Its *methyl ester* melts at 32°. *Cyclic Double-acid Amide* (1, 357), $C_6H_5.CH<\genfrac{}{}{0pt}{}{CO-NH}{NH-CO}>CH.C_6H_5$, melts with decomposition at 274° (B. 24, 4149). Its *nitrile* is a yellow oil, which gradually solidifies to a crystalline mass. It is very decomposable. It results from the action of ammonia upon mandelic nitrile.

Alkylic and phenylated phenylamido-acetic acids are obtained as the result of the action of methylamine, aniline, and similar bases upon phenylbrom-acetic acid (B. 15, 2031).

Of the alphylglycollic acids, mention may yet be made of p **Isopropyl-mandelic Acid**, prepared from cumic aldehyde, prussic acid, and hydrochloric acid. It, too, has been resolved by means of quinine into its active isomerides (B. 26, R. 89).

Phenyloxypropionic Acids, Phenyl-lactic Acids.—There are four possible structural isomerides. All are known and contain an asymmetric carbon atom:

CO_2H	CO_2H	CO_2H	CO_2H
$C_6H_5.COH$	$CHOH$	$C_6H_5.CH$	CH_2
CH_3	$C_6H_5.CH_2$	$CH_2.OH$	$C_6H_5.CHOH$
α-Phenyl-lactic Acid, Atrolactinic Acid	β-Phenyl-lactic Acid	α-Phenylhydracrylic Acid, Tropaic Acid	β-Phenylhydracrylic Acid.

1. **Atrolactinic Acid**, *α-Phenyl-lactic Acid*, $C_9H_{10}O_3 + 1\frac{1}{2}H_2O$, melts when in the hydrous state at 90°, and when anhydrous at 94°. It is obtained from α-bromhydroatropic acid when the latter is boiled with a soda solution, and by oxidizing hydroatropic acid with potassium permanganate. It is prepared synthetically from acetophenone, $C_6H_5.CO.CH_3$, by means of prussic acid and sulphuric acid or dilute hydrochloric acid (B. 14, 1980). When boiled with concentrated hydrochloric acid it decomposes into water and atropic acid.

Corresponding to atrolactinic acid are α-**chlor**- and α-**bromhydratropic acids**, melting at 73° and 93°, which are produced when it stands in contact with concentrated haloid acids (A. 209, 3). α-**Amidohydratropic Acid** sublimes, without melting, at 260° (B. 14, 1981).

2. **Tropic Acid**, *α-Phenylhydracrylic Acid*, is known in an inactive, decomposable and two optically active modifications.

Inactive tropic acid, melting at 117°, is obtained, together with tropine (see this) (A. **138**, 233; B. **13**, 254), on digesting (60°) the alkaloids atropine and hyoscyamine with baryta-water. It was made synthetically from atropic acid, the decomposition product of atrolactinic acid, by changing it with concentrated hydrochloric acid into β-chlorhydratropic acid, which boiling potassium carbonate converts into inactive tropic acid:

$$\underset{\text{Atrolactinic Acid}}{C_6H_5.\overset{CO_2H}{\underset{CH_3}{C}OH}} \longrightarrow \underset{\text{Atropic Acid}}{C_6H_5.\overset{CO_2H}{\underset{CH_2}{C}}} \xrightarrow{HCl} \underset{\beta\text{-Chlorhydratropic Acid}}{C_6H_5.\overset{CO_2H}{\underset{CH_2Cl}{CH}}} \xrightarrow[K_2CO_3]{H_2O} \underset{\text{Tropic Acid.}}{C_6H_5.\overset{CO_2H}{\underset{CH_2OH}{CH}}}$$

Lævo- and dextro-tropic acids, melting at 128° and 123°, can be separated by the fractional crystallization of their quinine salts. The dextro-quinine salt, more sparingly soluble in dilute alcohol, melts at 186°, and the lævo-salt at 178° (B. **22**, 2591).

β-Chlor- and β-Bromhydratropic Acids melt at 87° and 93°.

β-Amidohydratropic Acid melts at 119° (A. **209**, 3).

3. **β-Phenyl-lactic Acid**, *Benzylglycollic acid*, $C_6H_5.CH_2.CH.(OH).CO_2H$, melting at 97°, is derived from phenylacetaldehyde with prussic acid and hydrochloric acid, and from benzyltartronic acid upon heating it to 180°. Heated with dilute sulphuric acid, it decomposes into phenylacetaldehyde and formic acid.

Phenylalanine, *β-Phenyl-α-amidopropionic Acid*, $C_6H_5.CH_2.CH(NH_2).CO_2H$, sublimes without decomposition when it is slowly heated. Upon rapid heating it yields phenylethylamine and a *cyclic double-acid amide*, $C_6H_5.CH_2.CH.<{}^{CO.NH}_{NH.CO}>CH.CH_2.C_6H_5$, melting at 290° (I, 357; II, 252) (A. **219**, 188; **271**, 169). It is found, along with asparagine (I, 490), in the sprouts of *Lupinus luteus*, and is formed in the decay or by the chemical decomposition of albumen (B. **16**, 1711). It is prepared from its nitrile, the product of the action of ammonia upon the nitrile of β-phenyllactic acid, with hydrochloric acid; further, by the reduction of α-amidocinnamic acid (B. **17**, 1623), and of α-isonitroso-β-phenylpropionic acid (A. **271**, 169). **Benzoyl Phenyl-alanine**, from benzoylamidocinnamic acid by reduction, melts at 182° (A. **275**, 15).

o- and **p-Nitrophenyl-lactic Acids** are produced in the nitration of phenyllactic acid. When reduced the o-acid yields **oxyhydrocarbostyril** (pp. 214, 255), $C_6H_4\begin{cases}[1]CH_2—CH.OH \\ [2]NH—CO\end{cases}$, melting at 197°, and the p-acid, **p-amido-β-phenyl-lactic acid**, $NH_2[4]C_6H_4.CH_2.CH(OH)CO_2H$, melting with decomposition at 188°.

o-**Oxyphenyl-lactic Acid**, *Salicyl-lactic acid*, $HO[2]C_6H_4CH_2CH(OH)CO_2H$, is a syrup-like mass. It results from the action of sodium amalgam upon o-oxyphenyl pyroracemic acid (p. 259) (B. **18**, 1188). Its inner phenol alcohol anhydride is **hydrocoumarilic acid**, $C_6H_4\begin{cases}[1]CH_2.CH.CO_2H \\ [2]O—\!—\!—\!\rfloor\end{cases}$, melting at 118°. This is the reduction product of coumarilic acid (A. **216**, 166). **p-Oxyphenyl-lactic Acid** melts at 144° in the anhydrous condition. It is formed when an excess of nitrous acid acts upon p-amidophenylalanine (A. **219**, 226).

p-**Nitrophenylalanine**, $NO_2[4]C_6H_4CH_2.CH(NH_2)CO_2H$, decomposes at 240°. It is formed in the nitration of phenylalanine.

p-Amidophenylalanine, $NH_2[4]C_6H_4.CH_2.CH(NH_2).CO_2H$, is produced in the reduction of p-nitrophenylalanine and p-nitrophenyl-α-nitroacrylic acid.

Tyrosine, p-*Oxyphenyl-alanine*, $HO[4]C_6H_4.CH_2CH(NH_2)CO_2H$, melts at 235°. It occurs in the liver when its functions are disturbed, the spleen, the pancreas, and in stale cheese (τυρός), and is formed from animal substances (urea, horn, hair, albumen) on boiling them with hydrochloric or sulphuric acid; by fusion with alkalies or by putrefaction (together with leucine, aspartic acid, etc.). It may be prepared synthetic-

ally from p-amidophenylalanine by the action of one molecule of potassium nitrite upon the hydrochloric acid salt.

History.—Liebig discovered tyrosine upon fusing freshly prepared cheese with caustic potash (1846) (A. **57**, 127; **62**, 269). E. Erlenmeyer, Sr., and Lipp (A. **219**, 161) succeeded in synthesizing tyrosine, beginning with phenylacetaldehyde.

Synthesis of Tyrosine.—Phenylacetaldehyde (p. 189) and prussic acid yield the nitrile of phenyl-lactic acid. Ammonia changes the latter to the nitrile of phenylalanine, which hydrochloric acid converts into phenylalanine. The latter by nitration yields p-nitrophenylalanine, whose reduction product, *p-amidophenylalanine hydrochloride*, is changed by an equimolecular quantity of nitrous acid into *tyrosine*:

	CN	CN	CO_2H	CO_2H	CO_2H	CO_2H
CHO →	CHOH →	$CHNH_2$ →	$CHNH_2$ →	$CHNH_2$ →	$CHNH_2$ →	$CH.NH_2$
CH_2	CH_2	CH_2	CH_2	CH_2	CH_2	CH_2
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$C_6H_4[4]NO_2$	$C_6H_4[4]NH_2$	$C_6H_4[4]OH$
Phenyl-acetaldehyde	Nitrile of *Phenyl-*lactic Acid	Amido-phenyl-lac*tic Acid* Nitrile	Phenyl-alanine	p-Nitro-phenyl-*alanine*	p-Amido-phenyl-*alanine*	Tyrosine.

Properties and Deportment.—It dissolves in 150 parts of boiling water, and crystallizes *in delicate, silky needles. It dissolves in alcohol with difficulty, and is insoluble in* ether.

Mercuric nitrate produces a yellow precipitate, which becomes dark red in color if it be boiled with fuming nitric acid to which considerable water has been added (delicate reaction). Being an amido acid, tyrosine unites with acids and bases, forming salts. If it be heated to 270° it decomposes into carbon dioxide and oxyphenylethylamine, $C_6H_4(OH).CH_2.CH_2.NH_2$. When fused with caustic potash it yields paraoxybenzoic acid, ammonia and acetic acid. Putrefaction causes the formation of hydroparacoumaric acid, and nitrous acid converts the tyrosine into para-oxyphenyl-lactic acid (A. **219**, 226).

4. **β-Phenyl-hydracrylic Acid**, $C_6H_5.CH(OH).CH_2.CO_2H$, commonly called *phenyl-lactic acid*, results on boiling β-bromhydrocinnamic acid with water (A. **195**, 138), and in the reduction of benzoyl acetic ester, as well as by the addition of hypochlorous acid to cinnamic acid, and then reducing the resulting chlor-acid with sodium amalgam. The acid melts at 93°. When heated with dilute sulphuric acid it decomposes (like the aliphatic β-oxy-acids) at 190° into water and cinnamic acid (together with a little styrolene) (B. **13**, 304). When digested with the haloid acids it forms phenyl-β-haloid-propionic acids.

o-, m-, and p-**Nitrophenyl-lactic Acids**, or *-hydracrylic Acids*, $NO_2.C_6H_4CH(OH).CH_2.CO_2H$, melt at 126°, 105°, and 132°. The three isomerides result upon treating the three nitro-β-bromhydrocinnamic acids with sodium carbonate, when (in the cold) the o-, m-, and p-**nitrophenyl-lactic acid lactones**, $\overset{\quad\quad\quad O\,—\,CO}{NO_2C_6H_4\underset{|}{C}H.\underset{|}{C}H_2}$, melting at 124°, 98°, and 92°, are also produced. *These are the only β-lactones known* (B. **17**, 595).

The ortho-nitro-acid results, further, by oxidizing the aldehyde first produced with silver oxide (B. **16**, 2206). When heated to 190° with dilute sulphuric acid it yields o-nitrocinnamic acid. Its lactone decomposes on boiling with water into carbon dioxide and o-nitrostyrolene; it yields β-oxyhydrocarbostyril when reduced.

When the three nitro-acids are heated with alcoholic zinc chloride, we do *not get their lactones*, but their esters (B. **17**, 1659).

β-**Chlor-, brom-, and iodhydrocinnamic acids,** $C_6H_5 . CHX . CH_2 . CO_2H$, melt at 126°, 137°, and 120°. They are obtained from cinnamic acid or β-phenylacrylic acid by the addition of halogen hydrides in aqueous or glacial acetic acid solution (B. **11**, 1221), and from β-phenylhydracrylic acid (see this). When heated or boiled with water the free acids decompose, with previous formation of β oxyacids, into halogen hydride and cinnamic acid. When neutralized, even in the cold, with alkali carbonates they break down into haloid acid, carbon dioxide, and styrolene, $C_6H_5 . CH : CH_2$.

o-, m-, and p-**Nitro-β-bromhydrocinnamic Acids,** $NO_2C_6H_4CHBr . CH_2 . CO_2H$, are produced by the addition of hydrogen bromide in glacial acetic acid to the three nitrocinnamic acids (B. **17**, 596, 1494) (see also nitrophenyl-lactic acid lactone).

β-**Amidohydrocinnamic Acid,** $C_6H_5 . CH(NH_2)CH_2 . CO_2H$, melts at 120° (B. **17**, 1498; A. **200**, 97).

γ- and δ-*Oxyacids*.—γ-Oxyacids, beginning with the phenyloxybutyric acids, are known. They pass readily into their lactones. γ-**Phenyl-γ-oxybutyric Acid,** $C_6H_5 . CH(OH) . CH_2 . CH_2 . CO_2H$, melts at 75°, and slowly decomposes even from 65–70° into water and its lactone—**phenyl-butyrolactone,** $C_{10}H_{10}O_2$. The latter melts at 37° and boils at 306°.

It is obtained from β-benzoyl propionic acid (p. 261) (B. **15**, 889) and from phenylbrombutyric acid. Its lactone is formed on boiling phenylisocrotonic acid and phenylparaconic acid with dilute sulphuric acid (A. **228**, 178; B. **29**, R. 14).

α-**Phenyl-γ-oxyvaleric Acid,** only stable in the form of liquid lactone (B. **17**, 73).

δ-**Benzyl-γ-oxyvaleric Acid** melts at 101° and its *lactone* at 33° (A. **268**, 94).

β-**Benzyl-γ-oxyvaleric Acid** melts at 75° and its *lactone* at 86° (A. **254**, 215). It is obtained from benzal-lævulinic acid.

α-**Benzyl-δ-oxyvaleric Acid** (B **24**, 2447).

B. **Dioxyalcohol Acids** *are chiefly obtained by oxidizing the phenyl-olefine-carboxylic* acids with potassium permanganate (A. **268**, 44; **283**, 338). The two possible phenyl glyceric acids are known.

Atroglyceric Acid, *a-Phenylglyceric Acid*, $CH_2OH . C(C_6H_5)OH . CO_2H$, melting at 146°, results on boiling α, β-dibromhydroatropic acid with excess of alkalies, and from benzoyl carbinol by means of prussic acid and hydrochloric acid (B. **16**, 1292). It breaks down into CO_2 and phenylacetaldehyde upon heating.

Dibromhydratropic Acid, $CH_2Br . C(C_6H_5)Br . CO_2H$, melting at 115°, is produced when bromine acts upon atropic acid. It decomposes on boiling with water into acetophenone, CO_2, and HBr.

Styceric Acid, *β-Phenylglyceric Acid*, $C_6H_5 . CHOH . CHOH . CO_2H$, melting at 141° with decomposition (A. **268**, 37), is obtained by first getting the dibenzoyl ester and saponifying it, or by boiling phenyl-α-chlorlactic acid with water; also by oxidizing cinnamic acid with potassium permanganate. Heated above its melting point, it decomposes into phenylacetaldehyde, carbon dioxide, and water. Hydrobromic acid converts it into phenyl-β brom lactic acid (B. **16**, 1289). The **dibenzoyl-acid** melts at 187°.

The *dibenzoyl methyl ester* melts at 113°.

The *dibenzoyl ethyl ester* melts at 109° (B. **12**, 538).

p-**Nitrophenylglyceric Acid,** melting at 167°, is obtained from p-nitrophenylglycidic acid.

o-**Amidophenylglyceric Acid** melts at 218°.

Phenyl-α-chlorlactic Acid, $C_6H_5 . CH(OH)CH . Cl . CO_2H + H_2O$, melts at 56°, and when anhydrous at 86°. It results from the action of hypochlorous acid upon cinnamic acid. Sodium amalgam reduces it to phenyl-lactic acid, alkalies change it to phenylglycidic acid and phenylglyceric acid, while with fuming hydrochloric acid it yields phenyldichlorpropionic acid (B. **22**, 3140).

Phenyl-α-bromlactic Acid, $C_6H_5 . CH(OH) . CHBr . CO_2H + H_2O$, melts at 125° when anhydrous. It is formed on boiling phenyldibrompropionic acid with water (B. **13**, 310). It has been separated by means of cinchonine into two optically active components (B. **24**, 2831).

Phenyl-α-iodlactic Acid, $C_6H_5 . CH(OH) . CHI . CO_2H$, melts at 137° with decomposition. It results from the action of an aqueous chloriodine solution upon cinnamic

acid (B. **19**, 2464). o- and p-**Nitrophenyl-α-chlorlactic Acids** melt at 119° and 165°. The o-body is converted by sodium amalgam into indol (B. **13**, 2261; **19**, 2646).

o-**Nitrophenyl-α-bromlactic Acid** melts at 145° (B. **17**, 219).

Phenyl-α-amidolactic Acid, *Phenylserin*, $C_6H_5.CH(OH)CH(NH_2)CO_2H + H_2O$, decomposes, when anhydrous, at 119°. It results from the action of acids upon the body formed when sodium hydroxide acts upon benzaldehyde and glycocoll (A. **284**, 46).

Phenyl-β-chlorlactic Acid, $C_6H_5.CHCl.CH(OH)CO_2H$, melting at 141°, and **Phenyl-β-bromlactic Acid** are produced when fuming haloid acids act upon phenylglyceric acid (B. **16**, 1290). o- and p-**Nitrophenyl-β-chlorlactic Acids,** melting at 125° and 167°, are obtained by the action of fuming hydrochloric acid upon the corresponding glycidic acids (B. **19**, 2646).

o-**Nitrophenyl-β-bromlactic Acid** melts at 135° (B. **17**, 221).

Cinnamic Acid Dichloride, *α,β-Dichlorhydrocinnamic Acid*, $C_6H_5.CHCl.CHCl.CO_2H$, melting at 163°, results when chlorine acts upon cinnamic acid in carbon disulphide solution and on treating phenyl-α-chlorlactic acid with fuming hydrochloric acid (B. **14**, 1867).

Allocinnamic Acid Dichloride is an oil decomposable by strychnine into two optically active components (B. **27**, 2041).

Cinnamic Acid Dibromide, *α,β-Dibromhydrocinnamic Acid*, melting at 195°, yields CO_2, phenylacetaldehyde, cinnamic acid, and phenyl-α-bromlactic acid on boiling with water. *Strychnine resolves it into two optically active components* (B. **26**, 1664). The *methyl ester* melts at 117°. The *ethyl ester* melts at 69° (B. **22**, 1181).

Allocinnamic Acid Dibromide melts at 91–93°. It is separated into two optically active components by cinchonine (B. **27**, 2039). The *methyl ester* melts at 52–53°.

o- and p-**Nitro-α,β-dibromhydrocinnamic Acids** melt at 180° and 227°. The o- and p-*ethyl esters* melt at 71° and 110° (A. **212**, 151).

Phenylglycidic Acid, $C_6H_5.CH\overset{O}{—}CH.CO_2H$, separated from the sodium salt, is an oil solidifying at 0°. It results from the action of alkalies upon α- and β-chlorphenyllactic acids, as well as by the condensation of benzaldehyde with chloracetic ester (A. **271**, 137). Phenylglycidic acid is very unstable. It readily decomposes into CO_2 and phenylacetaldehyde. On boiling with water phenylglyceric acid is also produced. The optically active phenylglycidic acids are obtained in the form of sodium salts from the optically active phenyl-α-bromlactic acids.

o-**Nitrophenyl-glycidic Acid,** $NO_2[2]C_6H_4CH\overset{O}{—}CH.CO_2H + H_2O$, melts at 94°, and at 125° when anhydrous. It is produced when alcoholic potash acts upon o-nitrophenyl-lactic acid, or by the action of sodium hypochlorite upon o-nitrophenyllactic acid ketone (A. **284**, 135). It breaks down, on heating, into CO_2 and *indigo*. It yields anthranil and anthroxanaldehyde on boiling with water (p. 249) (B. **19**, 2649).

p-**Nitrophenyl-glycidic Acid** melts with decomposition at 186° (B. **19**, 2644).

C. **Trioxyalcohol Acids.**—*γ-Phenyltrioxybutyric Acid*, $C_6H_5[CH.OH]_3CO_2H$, passes readily into the *lactone*, melting at 115–117°; by reduction this yields phenyltetrose (p. 248). γ-Phenyltrioxybutyric acid is prepared by starting with the dibromide of cinnamic aldehyde cyanhydrin (B. **25**, 2556).

7. PHENYLPARAFFIN-ALDEHYDE CARBOXYLIC ACIDS.

As explained under the aliphatic unsaturated ketols, oxyolefine carboxylic acids and oxyketone carboxylic acids (I, 318), the oxymethylene derivatives are produced by the condensation of acetone, acetic ester, acetoacetic ester, and other bodies with formic ester in the presence of sodium ethylate. As these compounds conduct themselves in many respects like aldehydes, it was originally supposed that they contained the aldehyde group, and it was only their very pronounced acid character which led to considering them as *oxymethylene* compounds. It is rather remarkable that two isomeric esters are formed in the condensation of phenylacetic ester and formic ester by means of sodium ethylate. Both bodies yield the same derivatives with phenylhydrazine. The one is a liquid and the other a solid. The latter is distinguished from the former by its stronger

acid character. It changes to the liquid modification on being heated. Carbonic acid precipitates from alkaline solutions of the esters the liquid, more feebly acid modification, whereas when an excess of mineral acid is added it is the solid, more acid modification which separates (see nitrophenyl methane, p. 178). W. Wislicenus believes that it is the solid modification which corresponds to the real phenyl formylacetic ester (B. 29, 742).

Oxymethylenephenylacetic Ethyl Ester, $CH(OH):C(C_6H_5)CO_2C_2H_5$, is a liquid boiling at 144° (16 mm.). Ferric chloride imparts a violet color to it.

Phenylformylacetic Ethyl Ester, $CHO.CH(C_6H_5)CO_2C_2H_5$, melts at 70°, passing at the same time into the liquid isomeric ester.

8. PHENYLPARAFFIN-KETONE CARBQXYLIC ACIDS.

The acids belonging in this group can be arranged, like the aliphatic ketone-carboxylic acids, into α-, β-, and γ-ketone-carboxylic acids, and in each of these groups we can have sub-groups, depending upon whether the ketone group is in direct union with the benzene nucleus or not.

A. α **Ketone-carboxylic Acids** result from (1) the oxidation of ketones; (2) of glycols; (3) of ketone alcohols; (4) of alcohol carboxylic acids; (5) (nucleus-synthetic) from cyanides of the acid radicals by saponification with cold, concentrated hydrochloric acid; (6) from benzenes by the action of chloroxalic esters in the presence of aluminium chloride (B. 20, 2045).

Phenylglyoxylic Acid, *Benzoyl Formic Acid*, $C_6H_5CO\,CO_2H$, melting at 65° and isomeric with the phthalaldehydic acids, is obtained by oxidizing acetophenone with potassium ferricyanide (B. 20, 389), as well as by oxidizing phenyl glycol, benzoyl carbinol, and mandelic acid with dilute nitric acid:

$$\left.\begin{array}{l} C_6H_5.CO.CH_3 \\ C_6H_5.CH(OH).CH_2OH \\ C_6H_5.CO.CH_2OH \\ C_6H_5.CHOH.CO_2H \end{array}\right| \rightarrow C_6H_5.CO.CO_2H.$$

The acid was first prepared (in a nucleus-synthesis way) by saponifying benzoyl cyanide, its nitrile, obtained from benzoyl chloride and mercury, or silver cyanide (Claisen). Its ethyl ester is formed when ethyl chloroxalic ester acts upon mercury diphenyl, or upon benzene in the presence of $AlCl_3$.

The acid is very soluble in water, and when distilled decomposes into CO_2 and benzaldehyde. When mixed with benzene containing thiophene and sulphuric acid, it is colored deep red, afterward blue-violet; all its derivatives, and also isatin, react similarly.

Being a ketonic acid it unites with sodium bisulphite and with CNH (see phenyl tartronic acid). Sodium amalgam converts it into mandelic acid, and hydriodic acid into α-toluic acid.

Its *methyl ester* boils at 247°. Its *ethyl ester* boils at 257°. The α-*amide* melts at 90°. The β-*amide hydrate*, $C_6H_5.CO.CONH_2 + H_2O$, melts at 64°. The γ-*amide* melts at 134° (B. 12, 633; 20, 397). The *anilide*, from γ-benzil monoxime (see this) and PCl_5, melts at 63°.

Benzoyl Cyanide, $C_6H_5.CO.CN$, melting at 32° and boiling at 207°, is obtained in the distillation of benzoyl chloride with mercuric cyanide, and by the action of acetyl chloride (B. 20, 2196) upon isonitrosoacetophenone. Sodium in absolute alcohol con-

verts it into **polybenzoyl cyanide**, $(C_8H_5NO_2)x$, melting at 95° (J. pr. Ch. [2], **39**, 260). Alkalies change benzoyl cyanide to benzoic acid and potassium cyanide, while concentrated hydrochloric acid converts it into benzoyl-formic acid. **Chlorisonitrosoacetophenone**, *benzoylformoximic acid chloride*, $C_6H_5 . CO . C(:NOH)Cl$, melting at 131°, is produced in the chlorination of isonitrosoacetophenone (p. 249) (B. **26**, R. 313).

Phenylhydrazimethylene Carboxylic Acid, $C_6H_5 . C\left(<\begin{matrix}NH\\|\\NH\end{matrix}\right) . CO_2H$. The hydrazine salt melts at 119°. **Diphenylglyoxylic Acid Hydrazone**, $\begin{matrix}C_6H_5 . C(:N)CO_2H\\ \quad | \\ C_6H_5 . C(:N)CO_2H\end{matrix}$. Its diethyl ester melts at 138° (J. pr. Ch. [2], **44**, 567).

Phenylglyoxylic Acid Phenylhydrazone melts at 153° (A. **227**, 341).

(β-), **Syn-phenylglyoxylic Acid Oxime** melts at 147°. (α-), **Anti-phenylglyoxylic Acid Oxime, Isonitrosophenylacetic Acid**, $C_6H_5 . C(:NOH)CO_2H$, melts at 128° (B. **24**, 42). The *methyl ester* melts at 138°. The *dimethyl ester* melts at 56° (B. **16**, 519). **Benzoyl Cyanide Oxime**, $C_6H_5 . C(:NOH)CN$, melting at 129° (B. **24**, 3504), is obtained from benzyl cyanide by means of amyl nitrite and sodium or nitrous acid and sodium ethylate (A. **250**, 163; B. **28**, 1797).

Substituted Benzoyl Formic Acids.—o- and p-**Brombenzoyl Formic Acids** melt at 93°–103° and 108° (B. **25**, 3298, and **28**, 259).

o-**Nitrobenzoyl Formic Acid**, $NO_2 . C_6H_4CO . CO_2H + H_2O$, melts at 47°, and when anhydrous at 122°. The *amide* melts at 199°. The *nitrile* melts at 54° (B. **23**, 1577). The *oxime* when acted upon with water yields CO_2 and o-nitrobenzonitrile. Salicylic acid is produced when it is boiled with alkalies (B. **26**, 1252). It forms two isomeric *phenylhydrazones* (B. **23**, 2080).

m-**Nitrobenzoyl Formic Acid** melts at 77°. The *amide* melts at 151°. The *nitrile* melts at 230° (145 mm.) (B. **14**, 1186).

o-**Amidobenzoyl-formic Acid**, *Isatinic acid*, is produced on reducing o-nitrobenzoyl formic acid with ferrous sulphate and sodium hydrate, and in the action of alkalies on isatin. If it be separated from its lead salt by means of hydrogen sulphide, and evaporated under greatly reduced pressure at low temperature, it is obtained as a white powder. Digestion of its solution converts it at once into its lactam or lactime—

Isatin, *lactam of isatinic acid*, $C_6H_4\left\{\begin{matrix}[1]CO . CO\\ [2]NH—|\end{matrix}\right.$, or *lactime of isatinic acid*, $C_6H_4\left\{\begin{matrix}CO\\N\end{matrix}\right\rangle C . OH$ (?), melting at 201°. It was first obtained by oxidizing indigo. It consists of orange-red prisms. It dissolves in the caustic alkalies with the formation of salts. The solution, violet at first, soon becomes yellow, owing to the production of isatinates. Isatin acts at the same time like a ketone.

Its other methods of formation and its derivatives will be discussed later in connection with the hydroindol derivatives. The isatin derivatives referable to the lactam formula are designated pseudo- or ψ-derivatives, or n-derivatives,—*i. e.*, those in which the recently entered group is attached to nitrogen,—whereas the true isatin derivatives are referred to the lactime formula, because the latter appears to belong to free isatin.

Aceto-isatinic Acid, $CH_3 . CO . NH[2]C_6H_4 . CO . CO_2H$, melting at 160°, results upon treating acetyl-ψ-isatin (see this) with alkalies, and then with acids. **Benzoyl-isatinic Acid**, melting at 188°, is produced when benzoyltetrahydroquinoline is oxidized with $KMnO_4$ (B. **24**, 772).

Acetyl-isatin, $C_6H_4\left\{\begin{matrix}[1]CO . CO\\ [2]N—<_{CO . CH_3}\end{matrix}\right.$, melts at 141°. **Benzoyl Isatin** melts at 206°.

Anthroxanic Acid, $C_6H_4\left\{\begin{array}{l}[1]C\!=\!\!-CO_2H\\ [2]N\!>\!O\end{array}\right.$ (?), melting at 190°, results upon oxidizing anthroxan aldehyde (p. 250) with potassium permanganate (B. **16**, 2222).

p-Dimethylamidophenylglyoxylic Ester, $(CH_3)_2N.C_6H_4CO.CO_2C_2H_5$, melting at 187°, is obtained from dimethyl aniline and ethyl oxalic acid chloride (B. **10**, 2081).

o-Oxyphenylglyoxylic Acid, from isatinic acid (B. **26**, 221), melts at 43°. **p-Methoxyphenylglyoxylic Acid** melts at 89°.

Veratroyl-carboxylic Acid, $(CH_3O)_2[3,4]C_6H_3.CO.CO_2H$, melting at 138°, and **Piperonoyl-carboxylic Acid,** $(CH_2O_2)[3,4]C_6H_3CO.CO_2H$, melting at 148°, have been produced by the oxidation of anethol, of isoeugenol methyl ether, and of isosafrol (B. **24**, 3488).

Homologous Phenylglyoxylic Acids. — **m-Tolylglyoxylic Acid** yields so-called **Methyl Isatin,** $CH_3[5]C_6H_3\left\{\begin{array}{l}[1]CO.CO\\ [2]NH\text{---}|\end{array}\right.$, melting at 184°. This is obtained by boiling **p-methylisatin-p-tolylimide,** melting at 259°, the product of the action of dichloracetic acid upon p-toluidine, with hydrochloric acid (B. **16**, 2262; **18**, 198).

	M. P.	
p-Tolyl-glyoxylic Acid,	96°	(B. **14**, 1750; **20**, 2049).
(p-)[2,5] **Xylyl-glyoxylic Acid,**	70–80°	(J. pr. Ch. [2], **43**, 144).
(m-)[2,4] **Xylyl-glyoxylic Acid,**	85°	(J. pr. Ch. [2], **41**, 485).
(o-)[2,3] **Xylyl-glyoxylic Acid,**	92°	(B. **20**, 1766).
Mesityl-glyoxylic Acid,	112–116°	(B. **24**, R. 741).
[2,4,5] **Pseudocumylglyoxylic Acid,**	75°	(B. **24**, R. 741).
2,3,4,6 and 2,3,5,6-**Tetramethylphenylglyoxylic Acid,**		(B. **19**, 233; **20**, 3099).

Phenylpyroracemic Acid, $C_6H_5.CH_2.CO.CO_2H$, melts at 154° with evolution of carbon dioxide. It is formed when *a*-benzoylamidocinnamic acid (A. **275**, 8) is boiled with caustic alkali or hydrochloric acid, as well as by boiling phenyloxalacetic ester with dilute sulphuric acid (A. **271**, 163).

o-Oxyphenylpyroracemic Acid, $HO.C_6H_4.CH_2.CO.CO_2H$, is produced, like phenylpyroracemic acid, from *a*-benzoylamido-o-oxycinnamic acid and sodium hydroxide. Its lactone, *a-Oxohydrocumarin,* $C_6H_4\left\{\begin{array}{l}[1]CH_2.CO\\ [2]O\text{---}CO\end{array}\right.$ (?), melting at 152°, is produced when it is boiled with acids (B. **18**, 1187).

B. **Phenylparaffin-β-Ketone Carboxylic Acids** are produced (1) by a condensation, similar to the acetoacetic ester formation, from benzoic and fatty acid esters, acetophenone and carbonic acid esters, with alcohol elimination, in the presence of sodium alcoholate (see benzoyl acetic ester); (2) by the introduction of alphyl residues, by means of chlorides,—*e. g.*, benzyl chloride,—into acetoacetic ester (see benzyl-acetoacetic ester); (3) by action of benzaldehydes upon diazoacetic ester (see benzoyl acetic ester).

With hydroxylamine they yield oxime anhydrides, lactoximes or isoxazolons; and with hydrazine and phenylhydrazine, hydrazine anhydrides, lactazams or pyrazolons (1, 362).

Benzoyl Acetic Acid, $C_6H_5.CO.CH_2.CO_2H$, melts at 103° with decomposition into CO_2 and acetophenone. It breaks down in the same manner when it is boiled with dilute acids. It is obtained by saponifying its ethyl ester with caustic potash at the ordinary temperature. Ferric chloride imparts a violet-red coloration to its solution.

Benzoyl Acetic Ester, $C_6H_5.CO.CH_2.CO_2C_2H_5$, boils at 148° (11 mm.). (1) It was first prepared by dissolving phenyl-propiolic ester in sulphuric acid and then diluting with water (B. **17**, 66). (2) By

the action of sulphuric acid and water upon α-bromcinnamic ester (B. **19**, 1392). (3) It is most conveniently made by the action of dry sodium ethylate or sodium upon ethyl benzoate and acetic ester (B. **20**, 653, 2179). (4) Small quantities of the ester are produced when esters of carbonic acid act upon acetophenone together with sodium ethylate. (5) It is also formed when benzaldehyde is heated with diazo-acetic ester:

$$\left.\begin{array}{ll}
1. & C_6H_4 . C=C . CO_2 . C_2H_5 \xrightarrow{SO_4H_2} \\
2. & C_6H_5 . CH=CBr . CO_2 . C_2H_5 \xrightarrow{H_2O} \\
3. & C_6H_5 . CO_2C_2H_5 + CH_3 . CO_2 . C_2H_5 \xrightarrow{-C_2H_5OH} \\
4. & C_6H_5 . CO . CH_3 + C_2H_5O . CO_2 . C_2H_5 \longrightarrow \\
5. & C_6H_5 . COH + N_2 . CH . CO_2C_2H_5 \xrightarrow{-N_2}
\end{array}\right] \longrightarrow \underset{\text{Benzoyl Acetic Ester.}}{C_6H_5 . CO . CH_2 . CO_2 . C_2H_5}$$

Benzoyl-acetic ester volatilizes with steam without decomposition (A. **282**, 155). Its odor resembles that of acetoacetic ester.

It forms (1) with ammonia an addition product like that of aldehyde-ammonia; with amines it splits off water and yields imides—*e.g.*, β-**methylimidohydrocinnamic ester,** $C_6H_5C(NCH_3)CH_2 . CO_2 . C_2H_5$ (B. **29**, 105); with (2) hydrazine it yields 3-phenyl-pyrazolon; (3) with phenylhydrazine, diphenylpyrazolon; (4) with hydroxylamine, phenylisoxazolon; (5) with urea, phenyluracil; (6) with guanidine, imidophenyluracil; (7) with nitrous acid, the oxime; (8) with diazobenzene chloride, the phenylhydrazone of benzoyl glyoxylic ester (p. 261); (9) with PCl_5, β-chlorcinnamic chloride. Iodine converts its sodium compound into dibenzyl-succinic ester, while with the alkylogens homologous benzoyl-acetic esters result. The hydrogen atoms of the CH_2-group are also replaceable, step by step, by acid radicals. It yields β-ethoxycinnamic esters when acted upon with orthoformic esters. The *amide* melts at 112° (A. **266**, 332), and the *anilide* at 107° (A. **245**, 374).

Benzoyl Acetonitrile, *ω-Cyanacetophenone*, $C_6H_5 . CO . CH_2 . CN$, melting at 80°, is produced on boiling benzoylcyanacetic ester (p. 263) with water, on acting upon sodium oxymethylene acetophenone with hydroxylamine hydrochloride and sodium hydroxide (B. **24**, 133), and upon treating imidobenzoylacetonitrile or imidobenzoyl methyl cyanide with hydrochloric acid.

Imidobenzoyl Cyan-methane, $C_6H_5 . C(:NH)CH_2CN$, melting at 86°, results when sodium acts upon a dry ethereal solution of benzonitrile and methyl cyanide or acetonitrile (B. **22**, R. 327). When treated with hydroxylamine hydrochloride, the imido-group is replaced by the oximido-group, and the latter adds itself to cyanogen with the production of **phenylisoxazolonimide,** $\begin{array}{l} N\text{———}O \\ \| \qquad\quad | \\ C_6H_5C . CH_2 . C:NH \end{array}$, melting at 111° (B. **26**, R. 272).

p-**Nitrobenzoyl-acetic Acid,** $C_6H_4(NO_2) . CO . CH_2 . CO_2H$, melts at 135°, and is produced by heating p-nitrophenyl propiolic ester with sulphuric acid. It breaks down, on melting, into CO_2 and p-nitroacetophenone. o-Nitrophenyl propiolic ester is readily transposed into the isomeric isatogenic ester (B. **17**, 326).

Methylbenzoyl-acetic Ester, boiling at 226° (225 mm.), when treated with nitrous acid forms α-isonitrosopropiophenone (B. **21**, 2119). **Ethyl- and diethylbenzoyl-acetic ester** boil at 210° (90 mm.) and 223° (150 mm.).

Allyl-benzoyl-acetic Ester boils at 220° (100 mm.). **Benzoyltrimethylene Carboxylic Acid,** melting at 148°, decomposes at higher temperatures into CO_2 and *benzoyl-trimethylene* (pp. 23, 190) (B. **16**, 2128, 2136).

2,5-**Dinitrophenyl-** and 2,4,6-**Trinitrophenyl acetoacetic Ester,** melting at 94° and 98°, result from the action of 2,5-dinitrobrombenzene and 2,4,6-trinitrochlorbenzene (p. 68) upon sodium acetoacetic ester (A. **220**, 131; B. **22**, 990; **23**, 2720).

Benzylacetoacetic Ester, $C_6H_5 . CH_2 . CH<\begin{smallmatrix} CO . C_2H_5 \\ CO_2CH_3 \end{smallmatrix}$, is derived from sodium

acetoacetic ester and benzyl chloride (A. **204**, 179). It boils at 276° and by the ketone decomposition yields benzyl acetone (B. **15**, 1875) (p. 190); by the acid decomposition it forms phenylpropionic acid (p. 197).

D. γ- and δ-**Ketone Carboxylic Acids.**

β-**Benzoylpropionic Acid,** $C_6H_5.CO.CH_2.CH_2.CO_2H$, melting at 116°, is obtained (1) by the condensation of benzene and succinic anhydride by means of $AlCl_3$ (B. **20**, 1376); (2) by reducing β-benzoyl acrylic acid; (3) by the elimination of carbon dioxide from benzoylisosuccinic acid (p. 262), and (4) from phenacyl-benzoylacetic ester by the acid decomposition; (5) by boiling the HCN-addition-product of cinnamic aldehyde with dilute hydrochloric acid, and carefully saponifying the phenyloxycrotonic acid produced at first in the cold, which in the heat rearranges itself (B. **29**, 2582):

$$C_6H_5CH=CH.CH(OH)CN \longrightarrow C_6H_5CH=CH.CH(OH).COOH \longrightarrow C_6H_5.CO.CH_2.CH_2.COOH.$$

It dissolves with difficulty in hot water. Sodium amalgam reduces it to γ-phenylbutyrolactone.

Phosphorus pentasulphide converts the acid into phenyloxythiophene (B. **19**, 553). It yields two isomeric *oximes*, melting at 129° and 92° (B. **25**, 1932).

α-**Phenyl-lævulinic Acid,** $C_6H_5.CH{<}^{CO_2H}_{CH_2.CO.CH_3}$, melting at 126°, is derived from phenylacetosuccinic ester (B. **17**, 72; **18**, 790). β-**Benzyl-lævulinic Acid,** $C_6H_5.CH_2.CH{<}^{CH_2.CO_2H}_{CO.CH_3}$, from β-benzal-lævulinic acid (A. **254**, 202), melts at 98°. See benzalangelicalactone. β-**Phenyl-γ-acetobutyric Acid,** $C_6H_5.CH{<}^{CH_2.CO_2H}_{CH_2.CO.CH_3}$, melts at 83°. It is obtained from phenyldihydroresorcinol by the action of alkalies or acids (B. **26**, 2057; A. **294**, 322). Phenyldihydroresorcinol is again formed when its esters are condensed with sodium alcoholate.

9. PHENYL-ALCOHOL-KETONE CARBOXYLIC ACIDS.

Benzoyl Glycollic Acid, $C_6H_5.CO.CH(OH)CO_2H$, melts at 125° (B. **16**, 2133). **Phenyl-γ-keto-α-oxybutyric Acid,** $C_6H_5.CO.CH_2.CH(OH)CO_2H$, melting at 125°, is obtained from its trichloride, chloral acetophenone, $C_6H_5.CO.CH_2.CH(OH)CCl_3$, melting at 76° (B. **26**, 557).

10. DIKETONE CARBOXYLIC ACIDS.

Benzoyl Glyoxylic Acid, $C_6H_5.CO.CO.CO_2H$. The α-oxime and α-phenylhydrazone of the ethyl ester of this acid have been prepared by the action of nitrous acid and diazobenzene chloride (B. **21**, 2120) upon benzoyl-acetic ester (p. 259).

Benzoyl-isonitroso-acetic Ester, $C_6H_5.CO.C(:NOH)CO_2C_2H_5$, melts at 121°. **Benzoyl-α-phenylhydrazone-glyoxylic Ester,** $C_6H_5.CO.C(:N.NHC_6H_5)CO_2C_2H_5$, melts at 65°.

Quinisatinic Acid, o-Amidobenzoyl Glyoxylic Acid, $NH_2[2]C_6H_4CO.CO.CO_2H$, at 120° breaks down into water and its lactam or lactime. It is obtained by oxidizing β,γ-dioxycarbostyril with ferric chloride. Its lactam or lactime is—

Quinisatin, $C_6H_4\begin{cases}[1]CO.CO \\ [2]NH.CO\end{cases}$ or $C_6H_4\begin{cases}[1]CO.CO \\ [2]N=COH\end{cases}$, melting at 255–260° (B. **17**, 985).

Benzoyl Pyroracemic Acid, $C_6H_5.CO.CH_2.CO.CO_2H$, melting at 157°, is prepared from its *ethyl ester* (melting at 43°), produced in the condensation of acetophenone and oxalic ester (B. **21**, 1131). Ferric chloride imparts a blood-red color to the alcoholic solution of the ester.

When benzoyl chloride acts upon acetoacetic ester it produces **benzoyl acetoacetic ester,** $C_6H_5.CO.CH.(CO.CH_3).CO_2C_2H_5$. This decomposes into acetophenone and benzoyl acetone (B. **18**, 2131).

o-**Nitrobenzoyl-aceto-acetic Ester** (A. **221**, 323).

Acetophenone-acetoacetic Ester, $C_6H_5 . CO . CH_2 . CH . <^{CO_2H}_{CO . CH_3}$, melts at 130°-140°, with decomposition into CO_2 and acetophenone-acetone (p. 249). Its *ethyl ester* is produced by the action of ω-bromacetophenone upon sodium acetoacetic ester (B. **16**, 2866). Like acetophenone-acetone, the ester readily forms a furfurane derivative.

11. PHENYLPARAFFIN DICARBOXYLIC ACIDS.

The phenylparaffin dicarboxylic acids, like the aliphatic, saturated dicarboxylic acids, can be arranged into malonic acids, ethylene succinic acids, etc.

Phenylmalonic Acids.—**Phenyl Malonic Acid**, $C_6H_5 . CH(CO_2H)_2$, melts at 152°, splitting off CO_2 and forming phenyl acetic acid. Its *ester*, boiling at 171° (14 mm.), is formed from phenyloxalacetic ester by the elimination of carbon monoxide (B. **27**, 1091). **Dinitrophenylmalonic Ester**, $(NO_2)_2 . C_6H_3 . CH(CO_2C_2H_5)_2$, melting at 51°, is obtained by the action of bromdinitrobenzene upon sodium malonic ester (B. **21**, 2472; **22**, 1232; **23**, R. 460; **26**, R. 10).

2,4,6-**Trinitrophenylmalonic Ester**, *Picrylmalonic Ester*, $(NO_2)_3C_6H_2CH(CO_2C_2H_5)_2$, exists in two modifications, melting at 58° and 64° (B. **28**, 3066; **29**, R. 997).

Benzyl Malonic Acid, *β-Phenylisosuccinic Acid*, $C_6H_5 . CH_2 . CH(CO_2H)_2$, melting at 117°, is obtained from its ester, produced in the action of benzyl chloride upon sodium malonic ester, as well as by the reduction of benzal malonic acid (p. 288) (A. **218**, 139).

o- and p-**Nitrobenzyl-malonic Ester** (B. **20**, 434).—The o-acid is condensed by sodium hydroxide to n-oxy-α-indol-carboxylic acid (B. **29**, 639). **Methylbenzyl Malonic Acid** (A. **204**, 177).

Phenylsuccinic Acids.—**Phenyl-succinic Acid**, $\begin{matrix} C_6H_5 . CH . CO_2H \\ | \\ CH_2 . CO_2H \end{matrix}$, melting at 167°, results from ω-chlorstyrene, $C_6H_5 . CH : CHCl$, as well as from benzal malonic ester, by means of potassium cyanide (A. **293**, 338); by the decomposition of phenyl-acetsuccinic ester, by means of very concentrated caustic potash; from phenyl-ethane-tri-carboxylic acid (p. 264), and from the so-called hydro-cornicularic acid, $C_{17}H_{16}O_8$. Its *anhydride* melts at 54° (B. **23**, R. 573).

o-**Oxyphenylsuccinic Acid** melts with decomposition at 150°. It is obtained from coumarin and potassium cyanide (A. **293**, 366).

Phenyl-methyl-succinic Acids, $\begin{matrix} C_6H_5 . CH . CO_2H \\ | \\ CH_3 . CHCO_2H \end{matrix}$, have been obtained in two modifications, melting at 170° and 192° (B. **24**, 1876).

Benyzlsuccinic Acid, $\begin{matrix} C_6H_5 . CH_2 . CH . CO_2H \\ | \\ CH_2 . CO_2H \end{matrix}$, melts at 161°, and results from sodium ethan-tricarboxylic ester, or sodium ethan-tetracarboxylic ester by the action of benzyl chloride, etc. (B. **17**, 449), as well as by the reduction of phenyl-itaconic acid (B. **23**, R. 237). It forms an *anhydride*, melting at 102°.

12. PHENYL-ALCOHOL-DICARBOXYLIC ACIDS.

Benzyl Tartronic Acid, $C_6H_5 . CH_2 . C(OH)(CO_2H)_2$, melts at 143°, with decomposition into CO_2 and β-phenyl-lactic acid (p. 252). It results from the action of caustic potash on *benzylchlormalonic ester*, the product obtained from the interaction of benzyl chloride and sodium chlormalonic ester (A. **209**, 243). *α-Anilido-*, *Phenyl-hydrazido-benzylmalonic Ester*, etc., are produced by the addition of the respective bases to benzal-malonic ester (B. **28**, 1451; **29**, 813).

β-**Methoxybenzyl Malonic Acid**, $C_6H_5 . CH(OCH_3) . CH(CO_2H)_2$, melts at 115° with decomposition into methyl alcohol and benzal malonic acid, from whose ester the β-methoxybenzylmalonic ester is produced by addition of sodium methylate (B. **27**, 289).

Phenylmalic Acids.—α-**Phenyl-α-oxysuccinic Acid,** $\begin{matrix} C_6H_5 . C(OH)CO_2H \\ | \\ CH_2 . CO_2H \end{matrix}$, melting at 187°, is produced by the action of bromine, phosphorus and water upon phenylsuccinic acid.

α-**Phenyl-β-oxysuccinic Acid,** $\begin{matrix} C_6H_5 . CH . CO_2H, \\ | \\ CH(OH) . CO_2H \end{matrix}$, melting at 150–160°, results from the interaction of phenylformylacetic ester, prussic acid, and hydrochloric acid (B. 23, R. 573).

Phenyl-itamalic Acid may be obtained in the form of its *lactone acid*, **Phenyl-paraconic Acid,** $\begin{matrix} C_6H_5 . CH . CH—CO_2H \\ O——CO>CH_2 \end{matrix}$, melting at 109°, by heating benzaldehyde with sodium succinate and acetic anhydride (1, 492) (A. 256, 63). When phenyl-paraconic acid is boiled with alkalies it yields the salts of phenyl-itamalic acid. The latter, when in a free condition, immediately reverts to phenyl-paraconic acid. This, upon distillation, breaks down into carbon dioxide, phenylbutyrolactone (p 254) and phenylisocrotonic acid. A further product is α-naphthol (see this).

Phenyl-itaconic acid is produced when metallic sodium or sodium ethylate acts upon phenylparaconic esters (p. 289). Hydriodic acid reduces it to benzyl succinic acid and phenyl-butyric acid (B. 29, 15).

o-, m-, p-**Chlorphenyl-paraconic Acids** result from the condensation of monochlorbenzaldehydes with sodium succinate, and yield three chlorinated naphthols (B. 21, R. 733). **1,3,4-Dichlorphenylparaconic Acid,** melting at 138°, forms two dichlornaphthols (B. 29, R. 224).

α- and β-**Methylphenyl-paraconic Acids** are produced in the condensation of benzaldehyde with pyrotartaric acid, and yield methyl-α-naphthols (A. 255, 257).

α-**Phenyl-γ-valerolactone Carboxylic Acid,** $\begin{matrix} C_6H_5 . CH . CO \\ | \quad\quad\quad O \\ CO_2H . CH . CH—CH_3 \end{matrix}$, melting at 167°, is produced in the reduction of phenylaceto-succinic ester (B. 18, 791).

13. PHENYLKETONE DICARBOXYLIC ACIDS.

Benzoyl Malonic Ester, $C_6H_5 . CO . CH(CO_2 . C_2H_5)_2$, and o-**Nitrobenzoylmalonic Ester,** are produced by the action of benzoyl chloride and o-nitrobenzoyl chloride upon sodium malonic ester (B. 20, R. 381). The latter yields quinoline derivatives upon reduction (B. 22, 386).

Benzoyl Cyanacetic Methyl Ester, $C_6H_5 . CO . CH.<^{CO_2 . CH_3}_{CN}$, melting at 74°, is formed from cyanacetic methyl ester (1, 440) and benzoyl chloride. Its *ethyl ester*, melting at 41°, from benzoyl acetic ester and cyanogen chloride, yields cyanacetophenone on boiling with water (p. 258).

Benzoyl-Isosuccinic Ester, $C_6H_5 . CO . CH_2 . CH(CO_2C_2H_5)_2$, is obtained from ω-bromacetophenone and sodium malonic ester (B. 18, 3324).

Phenyl-oxalacetic Ester, $\begin{matrix} C_6H_5 . CH . CO . CO_2 . C_2H_5 \\ | \\ CO_2 . C_2H_5 \end{matrix}$, is formed from oxalic ester, phenylacetic ester, and sodium (B. 20, 592). See phenyl-malonic acid, p. 262.

Phenylcyanpyroracemic Ester, $\begin{matrix} C_6H_5 . CH . CO . CO_2C_2H_5 \\ | \\ CN \end{matrix}$, is obtained from oxalic ester, benzyl cyanide, and sodium (A. 271, 172). See phenylpyroracemic acid, p. 259.

Phenyl-acetosuccinic Ester, $\begin{matrix} C_6H_5 . CH . CO_2H \\ | \\ CH_3 . CO . CH . CO_2H \end{matrix}$, is formed from sodium aceto-acetic ester and phenylbromacetic ester (B. 17, 71).

Benzyl-aceto-succinic Ester, $\begin{matrix} C_6H_5 . CH_2 . CH . CO_2H \\ | \\ CH_3 . CO . CH . CO_2H \end{matrix}$, results from the interaction of sodium acetosuccinic ester and benzyl chloride (B. 11, 1058).

14. PHENYL-OXYKETONE DICARBOXYLIC ACIDS.

Ketophenylparaconic Ester, $\begin{matrix} C_6H_5 . CH . CH{-}CO_2C_2H_5 \\ | \qquad\quad > CO \\ O{-}{-}CO \end{matrix}$, (B. **26**, 2144).

15. PHENYLPARAFFIN TRICARBOXYLIC ACIDS.

Phenylcarboxyl-succinic Acid, Phenyl-ethane-tricarboxylic Acid.—Its ester is formed when phenylchloracetic ester acts upon sodium malonic ester (A. **219**, 31). The acid breaks down, on heating, into CO_2 and phenylsuccinic acid (B. **23**, R. 573).

16. PHENYLKETO-TRICARBOXYLIC ACIDS.

α- and *β*-**Benzoyltricarballylic Acids,** $C_6H_5 . CO . CH(COOH)CH(COOH)CH_2 . COOH$ and $C_6H_5COC(COOH)(CH_2COOH)_2$. Their esters are formed from chlorsuccinic ester and benzoylacetic ester, or from benzoylacetic ester with bromacetic ester and sodium ethylate (B. **29**, R. 788).

Addendum.—A number of compounds attach themselves to the phenylpolyalcohols and their oxidation products. They may be regarded as derived from the various classes of bodies which have just been described, by assuming, in addition to the one aliphatic side-chain, a second or more groups (mostly carboxyl groups) attached to the benzene ring. Most of the bodies belonging here are o-di-derivatives of benzene, o-phenylene derivatives, obtained in part from o-phthalic acid, and in part by the oxidation of derivatives of ortho-condensed hydrocarbons—*e. g.*, indene and naphthalene. Mention may be made of the subjoined compounds. Some of them are intimately related to the dicarboxylic acids, which have been discussed, carrying the one carboxyl group in the nucleus and the other in the side-chain.

17. PHENYLENE-OXYDICARBOXYLIC ACIDS.

o-**Carbomandelic Acid,** $CO_2H[2]C_6H_4 . CH(OH)CO_2H$, decomposes readily into water and a lactone carboxylic acid:

Phthalid-carboxylic Acid, $C_6H_4\begin{cases} CH . CO_2H \\ CO > O \end{cases}$, melting at 149°, and beyond 180° decomposing into carbon dioxide and phthalide. It is produced by reducing phenylglyoxyl-o-carboxylic acid (B. **18**, 381). It is quite soluble in water and crystallizes in leaflets.

Phthalid-acetic Acid, $C_6H_4\begin{cases} CH . CH_2 . CO_2H \\ CO > O \end{cases}$, melting at 150°, is derived from phthalylacetic acid by reduction (p. 289) (B. **10**, 1558, 2200).

Normeconine-acetic Acid, $(HO)_2[5,6]C_6H_2\begin{cases} [1]CH{-}CH_2 . CO_2H \\ [2]CO > O \end{cases}$, melting at 228°, results from the action of hydriodic acid upon **meconine-acetic acid,** $(CH_3O)_2[5,6]C_6H_2\begin{cases} [1]CH . CH_2 . CO_2H \\ [2]CO > O \end{cases}$. The latter is formed in the condensation of opianic acid with malonic acid, glacial acetic acid, and sodium acetate (B. **19**, 2295).

Dihydroisocoumarin-carboxylic Acid, $C_6H_4\begin{cases} [1]CH_2 . CH . CO_2H \\ [2]CO - O \end{cases}$, melting at 153°, is isomeric with phthalid-acetic acid. It is produced in the oxidation of dihydronaphthol (see this) with potassium permanganate (B. **26**, 1841).

Phthalid-propionic Acid, $C_6H_4\begin{cases} [1]CH{-}CH_2 . CH_2CO_2H \\ [2]CO > O \end{cases}$, melting at 140°, results from the reduction of phthalylpropionic acid (B. **11**, 1681).

o-Phenylene-aceto-glycol-lactone Acid, $C_6H_4\left\{\begin{array}{l}[1]CH(CO_2H)O \\ [2]CH_2\text{———}CO\end{array}\right. + 1\frac{1}{2}H_2O$, melting at 85°, is obtained from phenylene diacetic acid, bromine, phosphorus, and water (B. **26**, 223).

o-Carbophenylglyceric Acid Lactone, $C_6H_4\left\{\begin{array}{l}[1]CH(OH).CH.CO_2H \\ [2]CO\text{———}O\end{array}\right.$, melting at 202°, is produced when β-naphthoquinone is oxidized with a bleaching lime solution. When the lactone acid is heated with hydrochloric acid it loses water and becomes o-carbon-α-oxycinnamic acid lactone (B. **27**, 198).

18. PHENYLENE KETONE DICARBOXYLIC ACIDS.

o-Carbophenylglyoxylic Acid, *Phthalonic Acid,* $C_6H_4\left\{\begin{array}{l}[1]CO.CO_2H \\ [2]CO_2H\end{array}\right.$, melting at 138–140°, is formed in the oxidation of o hydrindene carboxylic acid (see this), naphthalene, α-naphthol, β-naphthol, and the oxy-quinone of β-phenylnaphthalene with potassium permanganate (A. **240**, 142). It yields o-carbo-mandelic acid upon reduction (p. 264).

Trichloraceto-benzoic Acid, $C_6H_4\left\{\begin{array}{l}[1]CO.CCl_3 \\ [2]CO_2H\end{array}\right.$, melting at 144°, and **Tribromaceto-benzoic Acid,** melting at 160°, result when chlorine or bromine, in glacial acetic acid, acts upon phthalylacetic acid (B. **10**, 1556).

o-Carbobenzoyl Acetic Acid, $C_6H_4\left\{\begin{array}{l}[1]CO.CH_2.CO_2H \\ [2]CO_2H\end{array}\right.$, melting at 90°, with decomposition into carbon dioxide and acetophenone-o-carboxylic acid (p. 238), is formed when phthalyl acetic acid is dissolved in an excess of caustic soda and precipitated with acids (B. **10**, 1553).

Cyanacetophenone-o-carboxylic Acid melts at 136° (B. **26**, R. 371).

Benzoyl-cyanacetoester-o-carboxylic Acid, $CO_2H[2]C_6H_4.CO.CH{<}^{CO_2C_2H_5}_{CN}$, melting at 121°, is produced by the action of soda upon phthalylcyanacetic ester (B. **26**, R. 370).

o-Carbobenzoyl-propionic Acid, $C_6H_4\left\{\begin{array}{l}[1]CO.CH_2.CH_2.CO_2H \\ [2]CO_2H\end{array}\right.$, melts at 137°.

The *double lactone,* $C_6H_4\left\{\begin{array}{l}C\text{—}CH_2.CH_2.CO \quad (\text{O—}\text{—}) \\ CO{>}O\end{array}\right.$, corresponding to this acid, is produced on heating succinic anhydride and phthalic anhydride with sodium acetate (B. **11**, 1680; **18**, 3119).

19. TRI- AND TETRA-CARBOXYLIC ACIDS.

Benzylmalon-o-carboxylic Acid, o-*Carbobenzylmalonic Acid,* $C_6H_4\left\{\begin{array}{l}CH_2.CH(CO_2H)_2 \\ CO_2H\end{array}\right.$, breaks down at 190° into hydrocinnam-o-carboxylic acid and CO_2. Its diethyl ester results from the reduction of phthalylmalonic ester (A. **242**, 37).

o-, m-, p-**Xylylene-dimalonic Tetra-ethyl Esters,** $C_6H_4[CH_2.CH(CO_2C_2H_5)_2]_2$, are produced in the reduction of the three corresponding **xylylenedichlor-dimalonic esters,** $C_6H_4[CH_2CCl(CO_2C_2H_5)_2]_2$, which are the products of the action of sodium chlormalonic ester upon the ω-xylylene dibromides (B. **21**, 31). The xylylene dimalonic acids break down, on heating, into phenylene dipropionic acids and $2CO_2$.

20. OXYTRI- AND PENTACARBOXYLIC ACIDS.

Phthalyl Diacetic Acid, $C_6H_4\left\{\begin{array}{l}C[CH_2.CO_2H]_2 \\ \diagdown \\ COO\end{array}\right.$, melting at 158°, is obtained from **phthalyl dimalonic acid,** $C_6H_4\left\{\begin{array}{l}C(CH)(CO_2H)_2)_2 \\ \diagdown \\ COO\end{array}\right.$ (A. **242**, 80).

21. KETONE TRICARBOXYLIC ACIDS.

2,6-Dicarbophenylglyoxylic Acid, $(CO_2H)_2[2,6]C_6H_3CO.CO_2H$, melting at 238°, is formed when naphthalic acid is oxidized with $KMnO_4$ (B. **26**, 1798). Hydriodic acid and phosphorus reduce it to 2-methylisophthalic acid (p. 242), and when heated it becomes 2-aldehydoisophthalic acid (p. 245), while more complete oxidation converts it into hemimellitic acid (B. **29**, R. 282).

Iregenone Di- and Tri-carboxylic Acids, $CH_3[4]C_6H_3\left\{\begin{matrix}[1]C(CH_3)_2CO_2H\\ [2]CO.CO_2H\end{matrix}\right.$ and $CO_2H[4]C_6H_3\left\{\begin{matrix}[1]C(CH_3)_2CO_2H\\ [2]CO.CO_2H\end{matrix}\right.$ (B. **26**, 2684).

MONO-NUCLEUS, AROMATIC SUBSTANCES, WITH UNSATURATED SIDE-CHAINS.

The benzene derivatives thus far considered contained saturated side-chains having carbon present in them. To these are attached the compounds having *unsaturated side-chains*—*e. g.* :

Phenylethylene, Styrolene,	$C_6H_5.CH:CH_2$	Phenyl Acetylene,	$C_6H_5C:CH$
Cinnamyl Alcohol, Styrone,	$C_6H_5.CH:CH.CH_2OH$	—	
Cinnamyl Aldehyde, . .	$C_6H_5.CH:CH.CHO$	—	
Cinnamic Acid, ...	$C_6H_5.CH:CH.CO_2H$	Phenyl Propiolic Acid, . . .	$C_6H_5C:C.CO_2H$.

They can, like the unsaturated aliphatic bodies, be converted by numerous additive reactions into saturated compounds, as has frequently been shown in the preceding sections.

Ia. OLEFINE BENZENES.

Phenyl Ethylene, Styrolene, *Vinylbenzene*, $C_6H_5.CH:CH_2$, boiling at 144°, occurs in storax (1–5 per cent.), from which it is obtained upon distillation with water. It also accompanies crude xylene in coal-tar (B. **23**, 3169, 3269). It is prepared (1) by the action of zinc-dust and glacial acetic acid upon phenylacetylene. Sodium and methyl alcohol will produce the same result (two hydrogen atoms are added) (B. **21**, 1184). (2) By heating cinnamic acid with lime (B. **23**, 3269) or with water to 200°. (3) By the action of alcoholic potash upon brom-ethyl benzene, and (4) by the condensation of acetylene, C_2H_2, upon application of heat. (5) From vinyl bromide, benzene and aluminium chloride (A. **235**, 331). (6) It is best obtained from β-brom-hydrocinnamic acid, which is immediately decomposed by a soda solution into styrolene, carbon dioxide and hydrobromic acid (B. **15**, 1983). It is a mobile, strongly refracting liquid, with an agreeable odor. Pure styrolene is optically inactive ; its sp. gr. = 0.925 at 0°.

Hydriodic acid converts styrolene into ethyl benzene, $C_6H_5.C_2H_5$; hydrochloric and hydrobromic acids change it to α-haloid ethyl benzenes (B. **26**, 1709), while with chlorine and bromine it yields α,β-dihaloid ethyl benzenes ; chromic acid or nitric acid oxidizes it to benzoic acid.

With xylene and sulphuric acid, styrolene forms β-phenyl-α-tolyl propane; and with phenol, oxydiphenylethane (B. **24**, 3889). Nitrous acid converts it into **styrolene nitrosites,** $C_6H_5 . C_2H_3 . (N_2O_3)$ (B. **29**, 356).

A. *Styrolenes containing the substituents in the side-group.*—The derivatives of styrolene substituted in the vinyl residue will be discussed immediately after styrolene itself.

Two series of monosubstituted styrolenes result from the replacement of vinyl hydrogen. They are known as α- and ω-substitution products:

α-Bromstyrolene, $C_6H_5CBr : CH_2$. ω-Bromstyrolene, $C_6H_5 . CH : CHBr$.

The *α-products* result on heating styrolene chloride (-bromide) alone, with lime, or with alcoholic potash. They possess a penetrating odor, causing tears. They yield acetophenone (B. **14**, 323) when they are heated with water (to 180°) or with sulphuric acid. α-**Chlor-styrolene** also results from acetophenone chloride (p. 189) when it is digested with alcoholic potash.

α-**Chlorstyrolene** boils at 190°.
α-**Bromstyrolene** " " 150-160° (75 mm.)

The *ω-products* are derived (along with phenylacetaldehyde) from the β-phenyl-α-chlor (brom-) lactic acids (p. 255), upon heating with water. ω-**Chlorstyrolene** is obtained also from ω-dichlor ethyl-benzene with alcoholic potash. ω **Bromstyrolene** is formed from dibrom-hydrocinnamic acid (p. 255) by boiling with water. When they are heated with water, phenylacetaldehyde results. They are oils having a hyacinth-like odor.

See, further, phenylacetylene (p. 268) and phenylpropiolic acid (p. 284).

Dichlorstyrolene, $C_6H_5 . CCl : CHCl$, boils at 221° (B. **10**, 533). **Dibromstyrolene** boils at 253° (B. **17**, R. 22). **Di-iodstyrolene,** *phenylacetylene di-iodide*, melting at 76°, is obtained from phenylacetylene and iodine (B. **26**, R. 18). **Tri-iod-styrolene,** *Phenyl tri-iod-ethylene*, $C_6H_5 . CI : CI_2$, melting at 108°, is obtained from phenyl iod-acetylene and iodine dissolved in CS_2 (B. **26**, R. 19).

ω-**Nitro-styrolene,** phenylnitro-ethylene, $C_6H_5 . CH : CH(NO_2)$, melting at 58°, is obtained by boiling styrolene with fuming nitric acid, by heating benzaldehyde with nitromethane, $CH_3(NO_2)$, and $ZnCl_2$ to 190° (B. **17**, 527), and by the action of fuming nitric acid upon phenyl-isocrotonic acid (B. **17**, 413), as well as by the action of NO_2 upon cinnamic acid, when the dinitro-compound, $C_6H_5 . C_2H_2(NO_2)_2 . CO_2H$, formed at first, decomposes (B. **18**, 2438; **29**, 357). It possesses a peculiar odor, provoking tears, is readily volatilized in aqueous vapor, and forms yellow needles. Dilute sulphuric acid decomposes it into benzaldehyde, carbon monoxide, and hydroxylamine.

Phenylnitropropylene, $C_6H_5 . CH : C(NO_2)CH_3$, melting at 63°, is obtained by the action of N_2O_3 upon phenylmethyl acrylic acid (B. **24**, 2773).

Phenylvinylamine, *ω-Amidostyrolene*, $C_6H_5 . CH : CHNH_2$, is very unstable. It is obtained by heating α-amidocinnamic acid (p. 276) (B. **17**, 1622), and from ω-nitrostyrolene (B. **26**, R. 677).

B. *Styrolenes substituted in the benzene nucleus.*—The three nitrostyrolenes are produced by the action of a cold soda solution upon the nitrophenylbrom-lactic acids (p. 255) or by boiling the β-lactones of the phenylbrom-lactic acids with water (B. **16**, 2213; **17**, 595).

o-, m-, p-**Nitrostyrolenes,** $NO_2C_6H_4CH : CH_2$, melt at +13°, —5° and +29°. o-**Amidostyrolene** is a very unstable, oily body. m-**Amidostyrolene,** boiling at 112–115° (12 mm.), is an oil, which polymerizes with ease. m-**Azostyrolene** melts at 38° (B. **26**, R. 677). p-**Amidostyrolene,** melting at 81°, is formed on heating p-amidocinnamic acid, and together with p-amidocinnamic acid in the reduction of p-nitrocinnamic ester (B. **15**, 1984).

C. *Styrolenes substituted both in the benzene nucleus and in the side-chain.*—PCl_5 converts o- and p-nitroacetophenones into liquid ortho- and

p-*nitro-α-chlorstyrolene*, $NO_2 . C_6H_4 . CCl : CH_2$, melting at 63° (A. **221**, 329).

o-**Nitro-ω-chlorstyrolene**, $NO_2 . C_6H_4 . CH : CHCl$, melting at 58°, is obtained from o-nitrocinnamic acid and hypochlorous acid (B. **17**, 1070).

o-**Amido-chlorstyrolene**, melting at 56°, yields indol when it is heated to 170° with sodium alcoholate; see also o-oxy-ω chlorstyrolene (p. 269). p,ω **Dinitrostyrolene** melts at 199° (B. **17**, R. 528).

Mention may be made of the following *homologues of styrolene*: m- and p-**Methyl Styrolenes**, $CH_3 . C_6H_4CH : CH_2$, boil at 164° and at 170–175° (B. **24**, 1332).

Allyl Benzene, $C_6H_5 . CH : CH . CH_3$, boiling at 174°, is formed when styrone is reduced with hydriodic acid (B. **11**, 670). **Isoallylbenzene**, *Propenyl Benzene*, $C_6H_5 . CH_2 . CH : CH_2$, boiling at 155°, is obtained from benzene, allyl iodide, and zinc-dust (A. **172**, 132).

I b. Acetylene Benzenes: Phenylacetylene, *Acetenyl Benzene*, $C_6H_5 . C : CH$, boiling at 139°, is produced (1) when α-brom-styrolene and (2) acetophenone chloride are heated to 130° with alcoholic potash; (3) also from phenyl propiolic acid (p. 284), on heating it with water to 120°, or upon distilling the barium or aniline salt (B. **29**, R. 797).

It is a pleasant-smelling liquid. It forms metallic compounds, like acetylene, with ammoniacal silver and copper solutions: $(C_6H_5 . C : C)_2Cu$, is bright yellow, $C_6H_5 . CH : CAg$ is white (B. **25**, 1096). The sodium compound, C_8H_5Na inflames in the air, and with carbon dioxide it yields phenyl propiolic acid. When phenyl-acetylene is dissolved in sulphuric acid and diluted with water, it yields acetophenone, while styrolene is produced on boiling it with acetic acid and zinc-dust (B. **22**, 1184).

Phenyliod-acetylene, $C_6H_5C : CI$, boils at 136° (22 mm.) (B. **26**, R. 20).

o-**Nitrophenyl Acetylene** and p-**Nitrophenyl Acetylene**, $C_6H_4<^{C : CH}_{NO_2}$, melting at 81–82° and 152°, are produced on boiling o-nitrophenylpropiolic acid and p-nitrophenylpropiolic acid with water.

o-**Amidophenyl Acetylene**, $C_6H_4(NH_2)C : CH$, is an oil with an odor resembling that of the indigo vat. It is produced in the reduction of o-nitrophenyl-acetylene with zinc-dust and ammonia, or with ferrous sulphate and potassium hydroxide, and in the decomposition of o-amidophenylpropiolic acid.

Phenylmethylacetylene, *Phenylallylene*, $C_6H_5 . C : C . CH_3$, boiling at 185°, is produced on boiling phenylbrompropylene with alcoholic potash (B. **21**, 276). **Phenylethylacetylene**, boiling at 201°, is obtained from sodium phenylacetylide and ethyl iodide, as well as from phenyliodacetylene and zinc ethide.

I c. Diolefine Benzenes.—p-**Divinylbenzene**, $C_6H_4(CH : CH_2)_2$, is a liquid with an odor like that of petroleum. It is produced when p-di-α-bromethylbenzene is heated with quinoline (B. **27**, 2528).

II a. OLEFINE PHENOLS.

Various representatives of this class occur in the vegetable kingdom: chavicol, chavibetol, estragol, anethol, eugenol, safrol, asarone, apiol, etc. All are phenol-like derivatives of *allyl-* and isoallyl- or *propenyl-benzene*. The *allyl* fatty derivatives occurring in the vegetable kingdom were *mustard oil* (1, 423) and *oil of garlic* (1, 150).

A. **Olefine Monoxybenzenes.—m-Vinylphenol**, $CH_2 : CH . C_6H_4 . OH$, boiling at 115° (16 mm.), is obtained from m-amidostyrolene (p. 267). o- and p-**Vinyl anisols**, $CH_2 : CH . C_6H_4 . O . CH_3$, boiling at 198° and 204°, have been obtained from the corresponding methoxycinnamic acids (B. **11**, 515).

o-Oxy-ω-chlorstyrolene, $HO . [2]C_6H_4 . CH : CHCl$, melting at 54°, is obtained from o-amido-ω-chlorstyrolene. Caustic potash converts it into cumarone (see this). **o-Thio-ω-chlorstyrolene**, $HS . C_6H_4 . CH : CHCl$; see benzothiophene.

Allyl- and Propenyl Phenols.—A very common property of the allyl phenols is their rearrangement, induced by hot alcoholic potash, into isomeric propenyl compounds:

Methyl-chavicol,	$CH_3O.C_6H_4.CH_2.CH : CH_2 \longrightarrow CH_3O.C_6H_4.CH : CH.CH_3$	Anethol.
Methyl Eugenol,	$(CH_3O)_2C_6H_3.CH_2.CH : CH_2 \rightarrow (CH_3O)_2.C_6H_3.CH : CH.CH_3$	Methyl Isoeugenol
Safrol, . .	$(CH_2O_2)C_6H_3.CH_2.CH : CH_2 \rightarrow (CH_2O_2).C_6H_3.CH : CH.CH_3$	Isosafrol
Apiol, . .	$\left.\begin{matrix}(CH_3O)_2\\(CH_2O_2)\end{matrix}\right\} .C_6H.CH_2.CH:CH_2 \rightarrow \left.\begin{matrix}(CH_3O)_2\\(CH_2O)_2\end{matrix}\right\} C_6H.CH:CH.CH_3$	Isoapiol.

The propenyl derivatives are distinguished from the allyl derivatives by higher specific gravities, higher melting points, and greater refractive power (B. **22**, 2747; **23**, 862). When the propenyl compounds are acted upon with nitrous acid, in glacial acetic acid, they yield *di-isonitrososuperoxides*, derivatives of α-diketones (see anethol). The allyl- and propenyl-phenols, when carefully oxidized with potassium permanganate, yield *phenol glycols* (p. 248) and *phenol-glyoxylic acids* (p. 259). See B. **29**, 676, etc., for the action of bromine and alkalies.

Chavicol, p-*Allyl Phenol*, $CH_2 : CH . CH_2[4]C_6H_4OH$, boils at 237° and occurs in the oil obtained from the leaves of *Chavica Betle*. It is a colorless oil with peculiar odor and its aqueous solution is colored blue by a drop of ferric chloride. *Methyl Chavicol* boils at 226°, and *Ethyl Chavicol* boils at 232° (B. **23**, 862).

Estragol occurs in estragonal oil (B. **27**, R. 46). It is isomeric with methyl chavicol. It boils at 215° (compare B. **29**, 344). Both bodies change to anethol when heated with alcoholic potash. The cause of the isomerism of these two compounds has not yet been explained.

p-Anol, p-*Propenyl Phenol*, $CH_3.CH : CH[4]C_6H_4OH$, melting at 92°, is prepared by heating anethol with caustic alkali (A. Suppl. **8**, 88).

Anethol, p-*Propenyl Anisol*, $CH_3 . CH : CH[4]C_6H_4 . O . CH_3$, melting at 21° and boiling at 232°, occurs in anise oil, from the seed of *Pimpinella Anisum*, in that from the seed of *Illicium anisatum*, in the fruit of *Anethum fœniculum*, and in estragonal oil. It is also formed from estragol and methyl chavicol (see above). It has been obtained synthetically from β-p-methoxyphenylmethacrylic acid; this would prove that its constitution is that of p-propenyl anisol (B. **10**, 1604). Chromic acid oxidizes it to anisic and acetic acids, while dilute nitric acid changes it to anisic aldehyde (p. 219). Methoxyphenylglyoxylic acid is produced on treating it with potassium permanganate (p. 259). See also di-isonitroso-anethol peroxide, p. 250. o- and p-*Propenyl Anisols* boil at 222° and 227° (B. **29**, R. 644).

B. **Olefine Dioxybenzenes.**—Of this group it is the olefine-3,4-dioxybenzenes which are almost exclusively known. They usually occur as ethers in plants, or are obtained by the breaking down of plant acids.

Hesperetol, *Vinyl*-3,4-*guaiacol*, $\left.\begin{matrix}HO[3]\\CH_3O[4]\end{matrix}\right\} C_6H_3 . CH : CH_2$, melting at 57°, is produced in the dry distillation of calcium isoferulate (p. 283) (B. **14**, 967).

Allyl-3,4-pyrocatechine is not known in a free condition. However, its three methyl ethers and its methylene ether have been found in ethereal oils.

Eugenol, *Allyl*-4,3-*guaiacol, Eugenic Acid*, $\left.\begin{matrix}HO[4]\\CH_3O[3]\end{matrix}\right\} . C_6H_3 . CH_2 . CH : CH_2$, is

an aromatic oil boiling at 247°. It is colored blue by ferric chloride. It occurs in the oil from *Eugenia caryophyllata*, in that from *Eugenia pimenta*, etc. Sodium amalgam reduces coniferyl alcohol to eugenol (p. 272) (B. **9**, 418). Potassium permanganate oxidizes it to homovanillin, vanillin, and vanillinic acid. It breaks down into acetic acid and protocatechuic acid when fused with potassium hydroxide (p. 227). See B. **27**, 2455; **28**, 2082, for the derivatives of eugenol.

Chavibetol, *Betel-phenol, Allyl-3,4-guaiacol*, $\left.\begin{matrix}HO[3]\\CH_3O[4]\end{matrix}\right\}C_6H_3.CH_2.CH:CH_2$, boiling at 254° (760 mm.), 131° (12 mm.), occurs in the ethereal oil obtained from the leaves of *Piper Betle* (J. pr. Ch. [2], **39**, 349; B. **23**, 862).

Eugenol Methyl Ether, *Allyl-3,4-veratrol*, $(CH_3O)_2[3,4]C_6H_3.CH_2.CH:CH_2$, boiling at 244°, is present in paracoto oil (A. **271**, 304), in the ethereal oil from *Asarum europæum* (B. **21**, 1060), and in *baye-oil*. It has been synthetically prepared from pyrocatechol dimethyl ether, allyl iodide, and zinc-dust (B **28**, R. 1055). Chromic acid oxidizes it to dimethyl protocatechuic acid or vetraric acid (p. 228). It forms isoeugenol methyl ether when heated with alcoholic potash. It also results when sodium eugenol or potassium chavibetol is treated with methyl iodide (J. pr. Ch. [2], **39**, 353).

Safrol, Shikimol, *Allyl-3,4-pyrocatechol methyleneether*, $CH_2<\begin{matrix}O[3]\\O[4]\end{matrix}\Big\}C_6H_3.CH_2.CH:CH_2$, melting at 8° and boiling at 232°, is present in the oil of *Sassafras officinalis*, and in that of *Illicium religiosum* or *Shikimino-Ki*. Potassium permanganate oxidizes it to methylene-p-,m-dioxybenzylglycol (p. 248), homopiperonylic acid (p. 229), and piperonoyl carboxylic acid (p. 259), which are further oxidized to piperonal and piperonylic acid (p. 229) (B. **24**, 3488; **28**, 2088). **Nitrosites** (see B. **28**, R. 1004).

Propenyl-3,4-pyrocatechol, isomeric with allyl-3,4-pyrocatechol, is not known in a free state. The propenyl pyrocatechol ethers: *isoeugenol, isoeugenol methyl ether*, and *isosafrol*, isomeric with the previously described allyl pyrocatechol ethers, are derived from it.

Isoeugenol, $\left.\begin{matrix}HO[4]\\CH_3O[3]\end{matrix}\right\}C_6H_3CH:CH.CH_3$, boiling at 260°, is formed when homoferulic acid (p. 283) is distilled with lime and upon heating eugenol with caustic potash or sodium alcoholate in amyl alcohol (B. **27**, 2580; Ch. C. **1897**, I, 384).

Isoeugenol Methyl Ether, *Propenyl-3,4-veratrol*, boiling at 263°, results upon heating eugenol methyl ether with alcoholic potash (B. **23**, 1165). Potassium permanganate oxidizes it to veratroyl carboxylic acid (p. 259) and veratric acid (B. **24**, 2877). It yields a glycol, melting at 88°, when it is carefully oxidized (p. 248).

Isosafrol, $CH_2<\begin{matrix}O[3]\\O[4]\end{matrix}\Big\}C_6H_3.CH:CH.CH_3$, boiling at 249°, is obtained from safrol by heating it with alcoholic potash, or with dry sodium ethylate. Potassium permanganate oxidizes it to a glycol (p. 248), melting at 101°, and piperonoyl carboxylic acid (p. 259). Chromic acid changes it to piperonal, artificial heliotropine (p. 220), from which it can be again reformed by condensation with propionic acid, and the splitting-off of CO_2 from the methylene-homo-caffeïc acid, which is first produced (p. 283) (B. **29**, R. 382). Sodium and alcohol reduce it to dihydrosafrol and m-propyl phenol (B. **23**, 1160).

C. **Olefine Trioxybenzenes.—Asarone**, *Propenyl-2,4,5(?)-trimethoxybenzene*, $(CH_3O)_3[2,4,5]C_6H_2.CH:CH.CH_3$, melting at 67° and boiling at 296°, separates from the ethereal oil of the root of *Asarum europæum*, in which it is present together with terpenes and eugenol. Potassium permanganate oxidizes it to trimethoxybenzaldehyde and a trimethoxybenzoic acid (p. 231), which breaks down into CO_2 and oxyhydroquinone methyl ether when it is distilled with lime (B. **23**, 2294).

Myristicine, *Butenyl-3,4,5-trioxybenzene methyl methylene ether*, $\left.\begin{matrix}(CH_2O_2)\\(CH_3O)\end{matrix}\right\}C_6H_2C_4H_7$, melting at 30°, results upon treating the high-boiling portions of *muscat nut oil* and *maci oil* with metallic sodium. It can be oxidized to ethers of a trioxybenzaldehyde and a trioxybenzoic acid (B. **24**, 3818).

D. **Olefine Tetraoxybenzenes.—Apiol**, *Allylapionoldimethylmethylene ether*, $(CH_3O)_2(CH_2O_2).C_6H.CH_2.CH:CH_2$, melting at 30° and boiling at 294°, occurs in pars-

ley seeds and in *Petroselinum sativum*. Potassium permanganate oxidizes it to ethers of a tetraoxybenzaldehyde and a tetraoxybenzoic acid. See also *apionol*, p. 166. Boiling potash changes it to the isomeride **isapiol**, melting at 56° and boiling at 304° (B. **25**, R. 908). An apiol, boiling at 162° (11 mm.), differing from the preceding only in the relative position of the methylene and methyl groups, occurs in the oil from *Anethum graveolens* (B. **29**, 1800).

II b. Acetylene phenetol, $CH : C . C_6H_4O . C_2H_5$ (A. **269**, 13).

III. PHENYLOLEFINE ALCOHOLS WITH THEIR OXIDATION PRODUCTS.

The chemistry of the phenylolefine alcohols, aldehydes, and ketones has not been fully developed. Their phenol-like derivatives will be discussed in immediate connection with the most important representatives of the class. The division in detail of the material into polyalcohols and their oxidation products, as was carried out with uni-nucleus benzene derivatives having oxygen-containing side-chains, is not feasible with uni-nucleus benzene derivatives having unsaturated oxygen-containing side-chains, because at present no representatives have been prepared for many classes of compounds which can be deduced theoretically. The bodies belonging here will, therefore, be introduced at the proper places in connection with the simple phenylolefine alcohols and their oxidation products.

1 (*a*). Phenylolefine Alcohols.

The two phenylvinyl alcohols possible theoretically are not known, and apparently are incapable of existence. The α-haloid styrenes become acetophenone upon replacing their halogen atom by hydroxyl, while the β-haloid styrenes yield phenyl acetaldehyde:

α-Chlorstyrene, $C_6H_5 . CCl : CH_2 \xrightarrow{H_2O} C_6H_5 . CO . CH_3$ Acetophenone

ω-Bromstyrene, $C_6H_5 . CH : CHBr \longrightarrow C_6H_5 . CH_2 . CHO$ Phenylacetaldehyde.

However, the corresponding ethyl ethers have been prepared:

β-Phenylvinyl-ethyl Ether, $C_6H_5 . CH : CH . O . C_2H_5$, boiling at 217°, is formed from ω-chlorstyrene (p. 267) and sodium ethylate (B. **14**, 1868). *α-Phenylvinylethyl Ether*, $C_6H_5C(OC_2H_5) : CH_2$, boiling at 209°, is obtained by splitting off alcohol from acetophenone acetal (p. 189) with heat, and is rearranged by heating under pressure into isomeric phenyl ethyl ketone (p. 189) (B. **29**, 2931).

Styrone, Cinnamyl Alcohol, *γ-Phenyl-allyl Alcohol*, $C_6H_5 . CH : CH . CH_2OH$, melting at 33° and boiling at 250°, occurs as cinnamic ester in liquid *Storax*, the sap of the *Liquidambar orientalis* tree, found in the southwestern portion of Asia Minor. When oxidized it becomes cinnamic aldehyde, cinnamic acid, and benzoic acid; see also stycerine, p. 248. **Styrylamine,** $C_6H_5 . CH : CH . CH_2NH_2$, boils at 236° (B. **26**, 1858).

1 (*b*). Oxyphenylolefine Alcohols.

Oxyphenylvinyl alcohols are not known, but *cumarone*, $C_6H_4\begin{cases}[1]CH : CH \\ [2]O \text{———}\end{cases}$, an inner anhydride, the cyclic ether of o-oxyphenylvinyl alcohol, has been made. It will be described later under the heterocyclic compounds.

Glyco-o-cumar-Alcohol, $C_6H_{11}O_5 . O . C_6H_4 . CH : CH . CH_2OH$, melting at 115°, has been formed from glyco-o-cumaraldehyde (see below).

Sec. Methyl-o-cumar-Alcohol, $HO . C_6H_4 . CH : CH . CH(OH)CH_3$, melts at 47°. See methyl-o-cumar-ketone, p. 272.

Coniferyl Alcohol, m-*Methoxy*-p-*oxystyrone*, $\left.\begin{matrix}HO[4]\\CH_3O[3]\end{matrix}\right\} C_6H_3 . CH : CH . CH_2OH$, melting at 73°, is formed from coniferine (see this), which emulsin decomposes into glucoses and coniferyl alcohol. Vanilline results from its oxidation (p. 219) and eugenol from its reduction (p. 270).

Cubebine, $CH_2 \langle \begin{matrix}O[4]\\O[3]\end{matrix} \rangle C_6H_3 . CH : CH . CH_2OH$, melting at 125°, is found in cubebs, the fruit of *Piper cubeba*.

2 (*a*). **Phenylolefine Aldehydes.**

Cinnamic Aldehyde, *β-Phenylacroleïn*, $C_6H_5 . CH : CH . CHO$, boiling at 247°, forms the chief constituent of cinnamon oil from *Persea cinnamomum*, and the oil from *Persea Cassia*, from which it can be extracted with acid sodium sulphite. The first product is the double derivative, $C_6H_5 . CH : CH . CH(OH)SO_3K$, which combines with a second molecule of mono-potassium sulphite to yield $C_6H_5 . CHSO_3K . CH_2 . CH(OH) . SO_3K + 2H_2O$, which dissolves with difficulty (B. 24, 1805). The aldehyde results from the oxidation of cinnamyl alcohol, in the dry distillation of a mixture of the lime salts of cinnamic and formic acids, and by the action of hydrochloric acid gas or sodium hydrate (B. 17, 2117), or sodium ethylate (B. 20, 657) upon a mixture of benzaldehyde and acetaldehyde.

Cinnamic aldehyde is a colorless, aromatic oil, which distils readily in aqueous vapor. When exposed to the air it oxidizes to cinnamic acid. It adds chlorine and bromine very readily. The dihaloid addition products change with ease into *α*-**Mono-chlor-** and *α*-**Monobromcinnamic Aldehydes,** $C_6H_5 . CH : CX . CHO$, melting at 35° and 72° (B. 24, 246).

α- and *β*-**Trithiocinnamic Aldehyde** melt at 167° and 213° (B. 24, 1452).

Hydro-cinnamide, $(C_9H_8)_3N_2$, melts at 106°.

Its *phenylhydrazone*, $C_6H_5 . CH : CH . CH(N_2H . C_6H_5)$, melts at 168°. The *syn-oxime* melts at 138.5°.

The *anti-oxime*, melting at 64°, is converted by hydrochloric acid gas in ethereal solution into the syn-oxime (B. 27, 3428). Isoquinoline is produced when the latter is heated with P_2O_5 (B. 27, 2795).

Nitrocinnamic Aldehydes are obtained from the aldehydes of the nitrophenyl-lactic acids (p. 248). o-, m-, and p-Nitrocinnamic aldehydes melt at 127°, 116°, and 141° (B. 18, 2335).

α-**Methylcinnamic Aldehyde,** $C_6H_5 . CH : C(CH_3)CHO$ (B. 19, 526, 1248).

2 (*b*). **Oxyphenylolefine Aldehydes.**

o-Cumaric Aldehyde, $HO[2]C_6H_4 . CH : CH . CHO$, melting at 133°, is produced by the action of emulsin upon *Glyco-o-cumaric aldehyde*, $C_6H_{11}O_5 . O . C_6H_4 . CH : CH . CHO$, melting at 190°, the condensation product of helicine (see this) and acetaldehyde (B. 20, 1931). It occurs as methyl ether in the oil of cassia (B. 28, R. 386). m- and **p-Acrylaldehydophenoxyl-acetic Acid,** $CO_2H . CH_2O . C_6H_4 . CH : CH . CHO$ (B. 19, 3049).

Piperonyl Acroleïn, $(CH_2O_2)[3,4]C_6H_3CH : CH . CHO$, melting at 70°, is obtained from piperonal, acetaldehyde, and sodium hydroxide (B. 27, 2958); see piperic acid.

3. **Phenyldiolefine Aldehydes.**

o-**Nitrocinnamenyl Acroleïn,** $NO_2C_6H_4 . CH : CH . CH : CH . CHO$, melts at 153° (B. 17, 2026).

4 (*a*). Phenylolefine Ketones.

The phenylolefine ketones are readily obtained from the corresponding aldehydes and methyl ketones by means of sodium hydroxide.

Benzal Acetone, *Benzylidene Acetone, Cinnamyl Methyl Ketone*, $C_6H_5 . CH : CH . CO . CH_3$, melting at 41° and boiling at 262°, is produced in the distillation of calcium cinnamate and acetate, as well as in the condensation of benzaldehyde and acetone with dilute sodium hydroxide (A. 223, 139).

It dissolves with an orange-red color in sulphuric acid. Its *phenylhydrazone*, melting at 156°, readily rearranges itself to 1,6-diphenyl-3-methylpyrazoline and 1,5-diphenyl-3-pyrazole (see this) (B. **20**, 1099). Its *oxime* melts at 115° (B. **20**, 923). Boiling sodium hypochlorite converts benzalacetone into cinnamic acid. Chloroform is eliminated at the same time. The nitration of benzalacetone produces the o- and p-nitro-derivatives. Benzalacetone and sodium malonic ester condense to phenyldihydroresorcylic ester (B. **27**, 2054, 2199).

o- and p-**Nitrobenzal Acetone** melt at 60° and 110°, respectively (p. 249). The o-body passes readily into indigo. α-Methyl-quinoline results from it by reduction. Water is simultaneously liberated.

Piperonylidene Acetone, $(CH_2O_2)C_6H_3CH:CH.CO.CH_3$, melts at 96° (B. **28**, R. 1009).

Cuminol Acetone (A. **223**, 147). **Allyl Acetophenone,** $C_6H_5.CO.CH_2.CH_2.CH:CH_2$, from allyl benzoyl acetic acid (B. **16**, 2132), boils at 236°.

4 (*b*). **Oxyphenylolefine Ketones.**

o-**Oxybenzal Acetone,** *Methyl-o-cumar-ketone*, $HO.C_6H_4.CH:CH.CO.CH_3$, melting at 139°, is obtained from salicylaldehyde, and also by the action of emulsin upon *glucomethyl-o-cumarketone*, $C_6H_{11}O_5.O.C_6H_4.CH:CH.COCH_3$, melting at 192°. The latter compound is a condensation product of helicine (see this) and acetone (B. **24**, 3180). o-, m-, and p-*Phenoxyacetic acid-acryl methyl ketones* melt at 108°, 122°, and 177° (B. **19**, 3056).

5. **Phenyldiolefine Ketones.**

Cinnamenyl Acetone, $C_6H_5.CH:CH.CH:CH.CO.CH_3$, melting at 68°, results from the condensation of cinnamic aldehyde and acetone. Its *oxime* yields a pyridine derivative upon dry distillation (B. **29**, 613). **Benzalmesityl Oxide,** $C_6H_5.CH:CH.CO.CH:C(CH_3)_2$, boils at 178° (14 mm.) (B. **14**, 351). **Piperonylene Acetone,** $(CH_2O_2)C_6H_3.CH:CH.CH:CH.CO.CH_3$, melts at 89° (B. **28**, 1193).

6. Phenylolefine Carboxylic Acids.

These acids arrange themselves into two distinct classes. The one class is derived from a saturated acid by substituting an unsaturated side-chain for hydrogen attached to the benzene nucleus—*e. g.*, *vinyl benzoic acid*. The second class comprises the phenylated *olefine monocarboxylic acids*.

A. **Phenylolefine Carboxylic Acids** having their CO_2H group attached to the nucleus.

o-**Vinyl Benzoic Acid,** $CH_2:CH[2]C_6H_4.CO_2H$. o-Vinyl benzoic acids, chlorinated in the vinyl residue and also in the benzene residue, have been obtained by the decomposition of chlorinated hydrindene and naphthoquinone derivatives (B. **27**, 2761; A. **275**, 347). m-**Vinyl Benzoic Acid,** melting at 95°, is formed from m-amidostyrolene (B. **26**, R. 677). o-, m-, and p-**Propenylbenzoic Acids,** $CH_2:C(CH_3).C_6H_4.CO_2H$, melt at 60°, 99°, and 161° (A. **219**, 270; **248**, 64; **275**, 160).

o-**Vinylphenyl Acetic Acid,** $CH_2:CH.C_6H_4.CH_2.CO_2H$. Derivatives of this acid, chlorinated in the vinyl residue, have also been obtained by the breaking-down of chlorinated ketohydronaphthalenes (B. **21**, 3555).

B. **Phenylolefine Carboxylic Acids** *with the carboxyl group in the unsaturated aliphatic side-chain.*

The true phenylolefine monocarboxylic acids may be obtained by the oxidation of corresponding alcohols and aldehydes, as well as by similar methods from the phenylparaffin monocarboxylic acids or fatty acids (1, 277). The nucleus-synthetic method, however, is far more important; it consists in the action of the sodium salt and the anhydride of a fatty acid upon an aromatic aldehyde (Perkin's reaction).

History.—As early as the year 1856 Bertagnini found that cinnamic acid was formed upon heating benzaldehyde with acetyl chloride. In 1865 W. H. Perkin, Sr., synthesized coumarin, the lactone of o-oxycinnamic acid (p. 281), by heating sodium salicylaldehyde with acetic anhydride. In 1875 Perkin gave this reaction an entirely different aspect by allowing sodium acetate and acetic anhydride to act upon salicylaldehyde. In this modified form the reaction acquired more general application.

Many chemists have assisted in the amplification of the Perkin reaction, which in consequence has become one of the most fruitful synthetic methods.

The course of the reaction has been made clear by the researches of v. Baeyer and O. R. Jackson, Conrad and Bischoff, Oglialoro, and especially by those of Fittig and his students, Jayne and Slocum (A. **215**, 97, 116; **227**, 48):

(1) In the condensation of aromatic aldehydes and fatty acids the carbon atom, combined with the carboxyl group, unites with the carbon of the aldehyde group.

(2) The reaction takes place with the aldehyde and the sodium salt of the fatty acid. The anhydride of the latter acts as a dehydrating agent.

(3) The condensation proceeds in two stages: (*a*) the union of the aldehyde and the sodium salt, as in the formation of aldol, with the production of the sodium salt of a β-oxyacid; (*b*) the exit of water from the β-oxyacid, resulting in the formation of the olefine carboxylic acid. In many instances the reaction was arrested in the first stage:

$$(a)\ C_6H_5.CHO + CH_3.CO_2Na \longrightarrow C_6H_5.CH(OH).CH_2.CO_2Na.$$
$$(b)\ C_6H_5.CH(OH)CH_2.CO_2Na \xrightarrow{-H_2O} C_6H_5.CH:CH.CO_2Na.$$

A second nucleus-synthetic method for the preparation of phenyl-olefine carboxylic acids consists in the condensation of benzaldehydes with fatty acid esters by means of sodium ethylate or metallic sodium (Claisen, B. **23**, 976):

$$C_6H_5.CHO + CH_3.CO.O.C_2H_5 \xrightarrow{-H_2O} C_6H_5.CH:CH.CO_2.C_2H_5.$$

Phenyl Acrylic Acids.—According to the structural theory, there are two possible isomerides, the α- and β-acids, which are known in cinnamic and atropic acids:

β-Phenyl Acrylic Acid, Cinnamic Acid, $C_6H_5.CH:CH.CO_2H$ α-Phenyl Acrylic Acid, Atropic Acid, $C_6H_5.C\begin{smallmatrix}\diagup CO_2H\\ \diagdown CH_2\end{smallmatrix}$.

From what was learned in connection with the alkyl acrylic acids we might well expect the existence of *one* unstable (labile) modification of cinnamic acid. However, not less than *three* unstable (labile) forms of the ordinary cinnamic acid (p. 276) have been observed: two among the alkaloids occurring in the synthesis of cocaine—*natural iso-cinnamic acid* and *allo-cinnamic acid* (Liebermann). The third variety is the artificial *isocinnamic acid* (Erlenmeyer, Sr., A. **287**, 1) formed in the reduction from alcoholic solution of the unstable (labile) α-bromcinnamic acid (the β-bromcinnamic acid of Glaser) with zinc-dust.

Cinnamic Acid, *β-Phenyl Acrylic Acid, Acidum cinnamylicum,* $C_6H_5.CH:CH.CO_2H$, melting at 133° and boiling at 300°, occurs in Peru and tolu balsams, in storax, and in some benzoïn resins; also, together with α- and β-truxillic acids, the natural isocinnamic and allocinnamic acids, in the decomposition products of the associated alkaloids of cocaine.

Formation.—It is produced (1) by the oxidation of its alcohol and its aldehyde; (2) by the reduction of phenylpropiolic acid with zinc-dust and glacial acetic acid (B. **22**, 1181); (3) *nucleus-synthesis*—from benzaldehyde: (*a*) with sodium acetate and acetic anhydride, (*b*) with acetic

ester and sodium ethylate (see above); (4) upon heating benzal chloride with sodium acetate. The latter reaction serves for the technical preparation of cinnamic acid (B. **15**, 969); (5) by heating benzalmalonic acid (p. 288); (6) its phenyl ester is produced when phenyl fumaric ester is heated (p. 148).

Properties and Deportment.—Cinnamic acid crystallizes from hot water in fine needles, from alcohol in thick prisms. It is soluble in 3500 parts of water of 17°, and readily in hot water. It may be purified by distillation under greatly reduced pressure, or by crystallization from petroleum benzine (A. **188**, 194).

Ferric chloride produces a yellow precipitate in solutions of the cinnamates.

Nitric acid and chromic acid oxidize it to benzaldehyde and benzoic acid. It is converted into phenylglyceric acid by potassium permanganate (p. 255). Fusion with caustic potash decomposes it into benzoic and acetic acids.

Being an unsaturated acid, cinnamic acid can readily take up hydrogen, hydrogen bromide, hydrogen iodide, bromine, chlorine, and hypochlorous acid, with the production of hydrocinnamic acid (p. 197), β-brom-, β-iodhydrocinnamic acid (p. 255), phenyl-α,β-dichlor-, α,β-dibrompropionic acid or cinnamic acid dichloride, cinnamic acid dibromide, and β-phenyl-α-chlorlactic acid (p. 255).

Cinnamic Acid Derivatives.—*Methyl Ester* melts at 33° and boils at 263°. *Ethyl Ester* boils at 271°. *Phenyl Ester* melts at 72° and boils at 206° (15 mm.); see cinnamic acid. *Pyrocatechol Ester* melts at 129° (B. **11**, 1220; **18**, 1945; **25**, 3533). *Styryl Ester*, *Styracine*, melts at 44°. The *chloride* melts at 35° and boils at 154° (25 mm.). The *anhydride* melts at 130° (B. **27**, 284). The *amide* melts at 141°. The *anilide* melts at 151°. The *nitrile* melts at 11° and boils at 254° (B. **15**, 2544; **27**, R. 262).

Haloid Cinnamic Acids Substituted in the Side-chain.—(*a*) *Phenyl monohaloid Acrylic Acids.* The structural theory provides for two isomeric monochlor-acrylic acids, but there are really two modifications for each of these structural isomerides. It is customary to distinguish them as α- and β-chlorcinnamic acid and allo-α- and allo-β-chlorcinnamic acid (B. **22**, R. 741; A. **287**, 1).

α-**Chlorcinnamic Acid,** $C_6H_5.CH:CCl.CO_2H$, melting at 137°, is formed (1) by the action of alcoholic potash on phenyl-α-,β-dichlorpropionic acid; (2) from benzaldehyde, sodium monochloracetate, and acetic anhydride; (3) from phenyl-α-chlorlactic acid by means of acetic anhydride and sodium acetate; (4) by the action of CrO_3 upon aldehyde (B. **24**, 249).

Allo-α-chlorcinnamic Acid, melting at 111°, is produced, together with α-chlorcinnamic acid, according to method 1.

β-**Chlorcinnamic Acid,** $C_6H_5.CCl:CH.CO_2H$, melting at 132.5°, and **Allo-β-chlorcinnamic Acid,** melting at 142°, are formed by the addition of hydrochloric acid to phenylpropiolic acid.

α-**Brom-cinnamic Acid,** $C_6H_5.CH:CBr.CO_2H$, melting at 130°, and **Allo-α-brom-cinnamic Acid,** melting at 120° (Glaser's β-brom-cinnamic acid), result when phenyl-α,β-dibrompropionic acid is acted upon with alcoholic potash. The latter, when heated, changes to the *higher*-melting α-brom-cinnamic acid. When it is treated with zinc-dust in alcoholic solution it yields "artificial isocinnamic acid," together with allo-cinnamic acid. The latter, very probably, is the primary product of the reaction, and is converted by the zinc bromide into the artificial isocinnamic acid. Both yield benzaldehyde upon oxidation.

β-**Brom-cinnamic Acid,** $C_6H_5.CBr:CH.CO_2H$, melting at 133°, and **Allo-β-brom-cinnamic Acid,** melting at 158.5°, are formed simultaneously upon the addition of hydrogen bromide to phenylpropiolic acid. The second acid, upon heating, changes to the *lower*-melting β-brom-cinnamic acid, and upon reduction yields not only cinnamic acid, but also "*artificial isocinnamic acid.*"

(*b*) *Phenyldihaloid Acrylic Acids* result from the addition of halogens to phenylpropiolic acid. **Dichlorcinnamic Acid,** $C_6H_5.CCl:CCl.CO_2H$, melts at 120° (B. **25**, 2665). α- and β-**Dibrom-cinnamic Acids** melt at 139° and 100° (B. **25**, 2665). **Di-iodcinnamic Acid** melts at 121° (B. **24**, 4113).

The unstable (*labile*) **modifications of Cinnamic Acid** (p. 274):

Natural Isocinnamic Acid melts at 45–47° (57°), monoclinic (B. **23**, 147).

Allo-cinnamic Acid melts at 66°, monoclinic (B. **27**, 2048).

Artificial Isocinnamic Acid melts at 43.5–46°, monoclinic (A. **287**, 7).

All the varieties crystallize in monoclinic forms, which show no relationship to one another. The ratio of axes and the magnitude of angles are entirely different. The crystals of the artificial isocinnamic acid are characterized by their remarkable decomposability, which disappears with the other (*labile*) modifications.

Cinnamic acid cannot be converted into any of its unstable (labile) modifications. Allo-cinnamic acid forms an aniline salt, melting at 83° and dissolving with difficulty in ligroïne. It can also be easily obtained from the natural and the artificial isocinnamic acid.

Thus far "natural isocinnamic acid," has only been found in the decomposition acids of the alkaloids associated with cocaine, where it occurs together with ordinary and allo-cinnamic acids. The *allo-cinnamic acid*, however, has also been obtained with much cinnamic acid from benzalmalonic acid, and together with "*artificial isocinnamic acid*" by reducing allo α- and allo-β-brom-cinnamic acid in alcoholic solution, as well as from both isocinnamic acids by means of aniline. When allo-cinnamic acid is treated with zinc and bromine in alcoholic solution it yields artificial isocinnamic acid. Chlorine and bromine convert it into allo-cinnamic acid dichloride and allo-cinnamic acid dibromide (p. 255), addition products, differing from cinnamic acid dichloride and cinnamic acid dibromide. Concentrated sulphuric acid converts the three unstable (labile) modifications into ordinary cinnamic acid.

When a benzene solution of allo-cinnamic acid is exposed to sunlight the allo-acid gradually changes to the ordinary cinnamic acid. The addition of a trace of iodine accelerates this transposition very materially (B. **28**, 1446).

The "natural isocinnamic acid" also changes to the ordinary cinnamic acid under the influence of small quantities of iodine, by exposure to sunlight, or upon boiling and by heating with water to 260° (B. **23**, 516).

Four polymeric dicinnamic acids have been discovered in the isomeric truxillic acids. It is very probable that they are diphenyltetramethylene dicarboxylic acids.

α-**Amidocinnamic Acid**, $C_6H_5.CH:C(NH_2).CO_2H$, decomposes, when rapidly heated, at 240–250°, with the production of phenylvinylamine. Its hydrochloride is produced upon heating its benzoyl-lactimide with hydrochloric acid to 120°. The acid itself may be liberated from the hydrochloride by means of sodium acetate or soda.

α-**Acetamido-cinnamic Acid**, $C_6H_5.CH:C(NHCO.CH_3).CO_2H + 2H_2O$, melts, when anhydrous, at 190° with decomposition. It is formed when sodium hydroxide acts upon acetlactimide. The amide of an isomeric (?) α-amidocinnamic acid, melting at 160°, results when ammonia acts upon phenyldibrompropionic acid ester or α-brom-cinnamic acid ester (B. **29**, R. 795).

α-**Acetamido-cinnam-lactimide**, $C_6H_5.CH:\overset{CO}{\overset{|}{C}}\!-\!\!>NCOCH_3$ melting at 146°, results from the action of acetic anhydride upon α-amidophenyl-lactic acid, and from glycocoll, benzaldehyde, sodium acetate, and acetic anhydride.

α-**Benzoylamido-cinnam-lactimide**, $C_6H_5.CH:\overset{CO}{\overset{|}{C}}\!-\!\!>N.CO.C_6H_5$, melts at 165°. It is produced in the condensation of hippuric acid and benzaldehyde with acetic anhydride and sodium acetate. See phenylpyroracemic acid (p. 259). When heated with dilute alkalies the lactimide changes to *a-benzoyl-amido-cinnamic acid*, which decomposes at 275° with the formation of phenylacetaldehyde (A. **275**, 1; **284**, 36).

Cinnamic Acids substituted in the benzene nucleus are isomeric with the corresponding monocinnamic acid derivatives, having side-chain substitutions.

1. *Monohaloid cinnamic acids* have been made from the three nitro-cinnamic acids as starting-out substances (B. **16**, 2040; **18**, 961; **25**, 2109).

o-, m-, and p-**Chlor-cinnamic Acids** melt at 200°, 176°, and 241°.

o- and m-**Brom-cinnamic Acids** melt at 212° and 178°.

o-, m-, and p-**Iod-cinnamic Acids** melt at 213°, 181°, and 255°.

2. **Nitro-cinnamic Acids.**—The introduction of cinnamic acid into nitric acid of specific gravity 1.5 leads to the formation of the ortho- (60 per cent.) and para-nitro acids. To separate them, cover the acid mixture with 8–10 parts of absolute alcohol, and conduct hydrochloric acid gas rapidly into the liquid, until complete solution ensues. On cooling, the para-ester separates. The pure esters are saponified with sodium carbonate or with dilute sulphuric acid, when the pure acids result (A. **212**, 122, 150; **221**, 265).

The three isomeric acids can be prepared from the corresponding nitro-benzaldehydes by means of the Perkin's reaction:

o-, m-, and p-**Nitro-cinnamic Acids** melt at 240°, 197°, and 286°.
o-, m-, and p-**Nitro-cinnamic Ethyl Esters** melt at 44°, 78°, and 138°.

Oxidation converts the three nitro-cinnamic acids into the three nitrobenzaldehydes (p. 186) and nitrobenzoic acids (p. 210). Bromine unites with o- and p-nitrocinnamic acids and their esters; see p. 255 and nitrophenylpropiolic acids.

3. *Amido-cinnamic Acids* can be prepared by reducing the three mononitrocinnamic acids with tin and hydrochloric acid. The reduction is better effected with ferrous sulphate in an alkaline solution (B. **15**, 2294; A. **221**, 266).

o-, m-, and p-**Amido-cinnamic Acids** melt at 158°, 181°, and 176°. When the diazo-bodies are boiled with haloid acids the haloid cinnamic acids, described above, are produced; but when they are acted upon with boiling water, the products are o-, m-, and p-*coumaric acids* (pp. 280, 282).

Derivatives of o-*Amido-cinnamic Acid.*—The *ethyl ester* is obtained by reducing o-nitro-cinnamic ester with tin and hydrochloric acid in alcoholic solution (B. **15**, 1422). It separates in fine yellow needles, melting at 77°.

o-**Ethyl Amido-cinnamic Acid,** $C_6H_4<^{CH:CH.CO_2H}_{NH.C_2H_5}$, is obtained when ethyl iodide and potassium hydroxide act upon o-amido-cinnamic acid (B. **15**, 1423). It melts at 125°.

Benzoyl-o-amido-cinnamic Acid, $C_6H_5.CO.NH.C_6H_4.CH:CH.CO_2H$, melting at 192°, results from the oxidation of N-benzoyltetrahydroquinaldine (B. **25**, 1263).

Carbostyril Formation.—Free o-amido-cinnamic acid differs from o-amidohydrocinnamic acid in deportment, in that when heated alone it does not give rise to an inner anhydride formation; it behaves like o-coumaric acid. The anhydride formation occurs, however, when o-amidocinnamic acid is heated with hydrochloric acid (B. **13**, 2070), or with 50 per cent. sulphuric acid (B. **18**, 2395). The resulting anhydride is carbostyril, discovered in 1852 by Chiozza, when he reduced o-nitrocinnamic acid with ammonium sulphide. It can be viewed both as a lactime and a lactam:

$$\text{Lactam formula, } C_6H_4\begin{cases}[1]CH:CH\\ [2]NH.CO\end{cases}; \quad \text{lactime formula, } C_6H_4\begin{cases}[1]CH:CH\\ [2]N\ :COH.\end{cases}$$

According to the second formula, carbostyril is nothing more than α-oxyquinoline; hence it will be discussed later, in conjunction with quinoline. This will also be done with the alkyl compounds derived from both formulas.

4. o-**Nitrosoethylamido-cinnamic Acid,** $NO.N(C_2H_5).C_6H_4CH:CH.CO_2H$, melts at 150°, with decomposition. It is obtained from o-ethyl-amido-cinnamic acid. When reduced it condenses to ethylisindazole-acetic acid (see this).

5. o-**Hydrazine-cinnamic Acid,** $NH_2.NH.C_6H_4.CH:CH.CO_2H$, melts at 171°, with decomposition into indazole, $C_6H_4<^{CH.NH}_{N\text{---}|}$ (see this), and acetic acid.

o-*Sulphohydrazine-cinnamic acid,* $SO_3H.NH.NH.C_6H_4CH:CH.CO_2H$, is formed when sodium sulphite acts upon the hydrochloride of o-diazocinnamic acid. Hot hydrochloric acid breaks it down into o-hydrazine-cinnamic acid and the lactam of this acid, $C_6H_4\begin{cases}[1]CH:CH.CO\\ [2]N(NH_2)\text{---}|\end{cases}$, melting at 127° (A. **221**, 274).

6. *Sulpho-cinnamic acids* are produced when fuming sulphuric acid acts upon cinnamic acid (A. **173**, 8). The m-derivative has been obtained by a nucleus-synthesis from m-benzaldehyde-sulphonic acid (p. 187).

Cinnamic Acids Substituted both in the Side-chain and in the Benzene Nucleus.—α- and β-**Nitro-o-amido-cinnamic Acids**, melting at 240° and 254°, have been prepared from o-amido-cinnamic acid. α,m-**Dinitro-cinnamic Acid**, $NO_2[3]C_6H_4 . CH : C(NO_2)CO_2H$, is formed when a mixture of nitric and sulphuric acids acts upon m-nitro-cinnamic ester (A. **229**, 224).

α,p-**Dinitro-cinnamic Acid**, p-*Nitrophenyl-α-nitroacrylic acid*, has been obtained from p-nitro-cinnamic acid (A. **229**, 224). Also consult ω,p-dinitrophenyl-ethylene (p. 267) and p-amidophenylalanine (p. 254).

Homologous Cinnamic Acids.—Cinnamic acids containing alkyl groups in the benzene residue are produced when alkylized benzaldehydes are condensed with sodium acetate and acetic anhydride. The three tolyl aldehydes yield o-, m-, and p-*methyl-cinnamic acids*, β,o-, m-, and p-*tolyl acrylic acids*, melting at 169°, 115°, and 196°. Cuminol yields p-*cumenyl-acrylic acid*, $(CH_3)_2CH[4]C_6H_4 . CH : CH . CO_2H$, melting at 158°. When the latter is nitrated it yields not only the p-nitro-acid, but also o-nitro-cumenylacrylic acid, which manifests the same reaction transpositions as o-nitro-cinnamic acid (B. **19**, 255).

α-*Alkyl substituted cinnamic acids* are produced in the condensation of benzaldehyde with sodium propionate or butyrate and acetic anhydride (A. **227**, 57).

α-**Methyl Cinnamic Acid**, α-*Benzal-propionic Acid*, β-*Phenylmethacrylic Acid*, $C_6H_5 . CH : C(CH_3)CO_2H$, melting at 78° and boiling at 288°, is also formed from benzyl propionic ester and metallic sodium (see p. 192 and B. **20**, 617). **Phenyl-angelic Acid**, α-*Ethyl Cinnamic Acid*, α-*Benzal-n-butyric Acid*, $C_6H_5 . CH : C(C_2H_5)CO_2H$, melts at 104° (B. **23**, 978).

Higher ω-phenyl-n-olefine carboxylic acids are produced by heating the lactone carboxylic acids, when carbon dioxide is expelled, and in the reduction of phenyl diolefine dicarboxylic acids.

Phenyl-iso-crotonic Acid, β-*Benzal-propionic Acid*, $C_6H_5 . CH : CH . CH_2 . CO_2H$, melts at 86° and boils at 302° with partial decomposition into water and α-naphthol. It is formed also by expelling CO_2 and rearranging phenylparaconic acid, as well as from phenyltrimethylene tricarboxylic acid (B. **25**, 1155) upon the application of heat. It unites with hydrogen bromide, forming γ-phenyl-γ-brombutyric acid, which yields phenyl-butyro-lactone with a soda solution. Boiling dilute sulphuric acid converts it directly into phenylbutyrolactone (p. 254).

α- and β-*Methylphenyl iso crotonic Acids* melt at 110° and 112° (A. **255**, 262). *Hydrocinnamenyl Acrylic Acid*, $C_6H_5 . CH_2 . CH : CH . CH_2 . CO_2H$, melting at 31°, is formed when sodium amalgam acts upon cinnamenyl acrylic acid (p. 285). The conversion of phenyl iso-crotonic acid and hydrocinnamenyl acrylic acid into isomeric acids by displacement of the double linkage, upon boiling them with sodium hydroxide (A. **283**, 309), is worthy of note:

$$C_6H_5 . CH : CH . CH_2 . CO_2H \longrightarrow C_6H_5 . CH_2 . CH : CH . CO_2H$$
αβ-Phenyl-crotonic Acid, m. p. 65°.

$$C_6H_5 . CH_2 . CH : CH . CH_2 . CO_2H \longrightarrow C_6H_5 . CH_2 . CH_2 . CH : CH . CO_2H$$
αβ-Phenylpropylidene Acetic Acid, m. p. 104°.

Atropic Acid, α-Phenylacrylic Acid, $C_6H_5 . C\begin{cases} CO_2H \\ CH_2 \end{cases}$, melts at 106°. This acid, structurally isomeric with ordinary cinnamic acid, results from tropic acid and atrolactinic acid (p. 252) when they are heated with concentrated hydrochloric acid or with baryta-water. It is sparingly soluble in cold water, easily in ether, carbon disulphide, and benzene, and distils with aqueous vapor. Chromic acid oxidizes it to benzoic acid; when fused with caustic alkali it yields formic and α-toluic acids; sodium amalgam converts it into hydro-atropic acid, and hydrochloric and hydrobromic acids change it to α- and β-halogen hydro-atropic acids (p. 252).

Protracted fusion, or heating with water or hydrochloric acid, converts atropic acid into two polymeric *isatropic acids*, *diatropic acids*, $(C_9H_8O_2)_2$ (melting at 237° and 206°),

which bear the same relation to atropic acid that the truxillic acids sustain to cinnamic acid (B. **28**, 137).

Methyl Atropic Acid, $C_6H_5.C\begin{cases}CH.CH_3\\CO_2H\end{cases}$, melts at 135°, and is obtained from phenyl acetic acid and paraldehyde by the action of acetic anhydride (B. **19**, R. 251).

a-**Phenyl-allyl-acetic Acid**, $C_6H_5.CH(CH_2.CH:CH_2)COOH$, boiling at 200°, has been obtained from phenyl-allyl-malonic acid, and its *nitrile* from benzyl cyanide, allyl iodide, and caustic soda (B. **29**, 2601).

7. Oxyphenyl-olefine Carboxylic Acids.

A. **Monoxyphenyl-olefine Carboxylic Acids.**—*Formation*: They are obtained (1) from the corresponding amidophenyl-olefine carboxylic acids upon boiling the diazo-compounds with water (B. **14**, 479); (2) by a nucleus-synthesis, when the phenol aldehydes are heated with the sodium salts and anhydrides of the fatty acids (Perkin's reaction, pp. 274, 278).

The following nucleus-syntheses (v. Pechmann) lead to the inner anhydrides or δ-lactones of the o-oxycinnamic acids, the so-called coumarins: (3) the action of sulphuric acid upon phenol and malic acid, when it is very probable that the first product is the half-aldehyde of malonic acid, which condenses with the phenol.

(4) When sulphuric acid is allowed to act upon phenol and acetoacetic ester or mono-alkyl acetoacetic esters:

$$(3)\ C_6H_4\begin{cases}H + CO_2H.CH(OH).CH_2\\ OH \qquad\qquad HO\,CO\end{cases} \longrightarrow C_6H_4\begin{cases}[1]CH:CH\\ [2]O\text{—}CO\end{cases} \quad \text{Coumarin}$$

$$(4)\ C_6H_4\begin{cases}H + CH_3.CO.CH_2\\ OH \qquad C_2H_5O\,CO\end{cases} \longrightarrow C_6H_4\begin{cases}[1]C(CH_3):CH\\ [2]O\text{———}CO\end{cases} \quad \beta\text{-Methyl-coumarin.}$$

The first members of this series are the monoxy-cinnamic acids, obtained by method 1 from the three amido-cinnamic acids. o-Oxycinnamic acid or o-coumaric acid particularly is especially important. The δ-lactone *coumarin* corresponds to it. When coumarin is acted upon with bases, salts are formed which are isomeric with the o-coumarates. Isomeric dialkyl ethers are obtained from these isomeric salts.

The salts and ethers of coumarin are also designated as *a*-coumarates, and those of o-coumaric acid as the β-coumarates—salts and ethers. The cause of this isomerism is very probably dependent upon the fact that the lactone ring is still present in the salts and ethers of coumaric acid.

o-Coumaric Acid,	$C_6H_4\begin{cases}CH:CH.CO_2H\\OH\end{cases}$	Coumarin	$C_6H_4\begin{cases}CH:CH\\O\text{—}CO\end{cases}$
Dimethyl Ether of o-Coumaric Acid,	$C_6H_4\begin{cases}CH:CH.CO_2CH_3\\O.CH_3\end{cases}$	Dimethyl Ether of Coumarinic Acid,	$C_6H_4\begin{cases}CH:CH\\O\text{—}C(OCH_3)_2.\end{cases}$

When the hydrogen atom in coumarin, occupying the o-position with reference to phenol-oxygen, is replaced by the nitro-group, *free nitrocoumarinic acid* may be liberated from the salts.

This acid is distinguished from free 3-nitro-coumaric acid in that by the exit of water it reverts to 3-nitrocoumarin. Both acids have corresponding dialkyl esters:

3-*Nitrocoumaric Acid*, $NO_2[3]C_6H_3\begin{cases} CH:CH.CO_2H \\ OH \end{cases}$ 3-*Nitrocoumarinic Acid*, $NO_2[3]C_6H_3\begin{cases} CH:CH \\ O—C(OH)_2. \end{cases}$

The cause of the difference in the ethers of o-coumaric and coumarinic acids whenever their structure was similar, has also been attributed to the different position of the atom groups in space:

$$\begin{array}{l} HC.CO_2R \\ \| \\ RO.C_6H_4.CH \end{array}\quad \begin{array}{c}\text{o-Coumaric}\\ \text{Dimethyl Ether}\\ \text{(axially-symmetric)}\end{array} \qquad \begin{array}{l} HC.CO_2R \\ \| \\ HC.C_6H_4.OR \end{array}\quad \begin{array}{c}\text{Coumarinic}\\ \text{Dimethyl Ether}\\ \text{(plane-symmetric).}\end{array}$$

This latter hypothesis, however, does not explain the varying deportment of the isomeric dimethyl ethers of 3 nitro-coumaric acid and 3-nitro-coumarinic acid. When 3-nitro-coumaric dimethyl ether is saponified with a soda solution the methyl ether-acid results; whereas 3-nitro-coumarinic dimethyl ether, under like treatment, yields 3-nitro-coumarinic acid. If the difference, with similar linkage relations, of the isomeric dimethyl ethers were solely due to spacial arrangement, then the varying behavior of the o-nitro-coumarinic dimethyl ester could be neither anticipated nor explained; whereas it would be obvious if the o-nitro-coumarinic dimethyl ester were regarded as a kind of carbonic acid ester (A. **254**, 181):

$$NO_2[3]C_6H_3\begin{cases} CH:CH.CO_2.CH_3 \\ OCH_3 \end{cases} \longrightarrow NO_2C_6H_3\begin{cases} CH:CH.CO_2H \\ OCH_3 \end{cases}$$

$$NO_2[3]C_6H_3\begin{cases} CH:CH \\ O—C(OCH_3)_2 \end{cases} \longrightarrow NO_2C_6H_3\begin{cases} CH:CH \\ O—C(OH)_2. \end{cases}$$

Coumarin, its homologues and derivatives, will be arranged and treated as a group after o-coumaric acid.

o-Oxycinnamic Acid, o-Coumaric Acid, $HO[2]C_6H_4CH:CH.CO_2H$, melting at 208°, and isomeric with hydrocoumarilic acid, phenyl-pyroracemic acid, etc., occurs in *Melilotus officinalis*, together with o-hydro-coumaric acid, and in the leaves of *Angrecum fragans*. Nitrous acid converts o-amido-cinnamic acid into coumaric acid. It is most readily prepared by boiling coumarin for some time with concentrated potassium hydroxide, or, better, with sodium ethylate (B. **18**, R. 28; **22**, 1714). Its acetyl derivative is obtained from salicylic aldehyde and sodium acetate.

Ortho-coumaric acid is very easily soluble in hot water and in alcohol. It does not volatilize with steam. The free coumaric acid heated alone does not yield coumarin, but only when treated with acetic chloride or anhydride. Sodium amalgam converts it into melilotic acid, and fusion with potassium hydroxide into salicylic and acetic acids.

2-Methoxy-cinnamic Acid (β), $CH_3O[2]C_6H_4[1]CH:CH.CO_2H$, melting at 182°, is produced by the action of sodium acetate and acetic anhydride upon salicylaldehyde methyl ether, and by the rearrangement of methyl coumarinic acid (see this). Sodium amalgam reduces it to melilotic acid methyl ether, while bromine changes it to methyl-ether-dibrom-melilotic acid. **o-Coumaric Dimethyl Ether** (β), $CH_3O[2]C_6H_4[1]CH:CH.CO_2CH_3$, boiling at 293°, is obtained from the previously described acid chloride by means of methyl alcohol. **Acet-o-coumaric Acid,** $CH_3.CO.O[2]C_6H_4$.-

CH : CH . CO_2H, **melting at 149°, is obtained from salicylaldehyde, acetic anhydride, and sodium acetate** (B. **20**, 284); see coumarin.

3-**Nitro-coumaric Acid** (β), $NO_2[3]C_6H_3[2](OH)CH : CH . CO_2H$, is formed by the protracted heating of the dimethyl ether with sodium hydroxide. It suffers no change when heated with water, alcohol, or hydrogen bromide (distinction from 3-nitro-coumarinic acid). The *methyl ether-acid*, melting at 193°, is formed from 3-nitro-salicyl-aldehyde methyl ether, and from the *dimethyl ether*, melting at 88°, by the action of soda (see above). This latter ether is produced when methyl iodide acts upon the silver salt of the methyl ether-acid (B. **22**, 1710).

Coumarin, $C_6H_4\begin{cases}[1]CH : CH \\ [2]O —— CO\end{cases}$, melting at 67° and boiling at 290°, occurs in *Asperula odorata*, in the Tonka beans (from *Dipterix odorata*), and in *Melilotus officinalis*. It is artificially prepared by heating aceto-o-coumaric acid (B. **10**, 287), the reaction-product, resulting from acetic anhydride and sodium salicylaldehyde (A. **147**, 230), or from the action of acetic anhydride and sodium acetate upon salicylaldehyde (Perkin, Sr., B. **8**, 1599). It has the agreeable odor of *Asperula*, and is applied in perfumery for the preparation of the *Asperula* essence.

Coumarin dissolves rather easily in hot water, and very readily in alcohol and in ether. It dissolves in caustic potash with a yellow color, the first product being potassium coumarinate, from which carbon dioxide separates coumarin. Boiling, concentrated caustic potash changes it to potassium coumarate. In aqueous solution it is reduced by sodium amalgam to melilotic acid (p. 226). When it is digested with an aqueous-alcoholic solution of potassium cyanide, hydrocyanic acid is added, and upon subsequent saponification o-oxyphenylsuccinic acid is formed (A. **293**, 366).

Coumarin Monomethyl Ester-acid, melting at 88°, and **Coumarinic Dimethyl Ester**, boiling at 275° (Constitution, p. 280), result when sodium coumarin is heated to 150° with methyl iodide. When heated both compounds change to the corresponding o-coumaric acid derivatives. The methyl ether-acid when exposed in alcoholic solution to sunlight also passes into the isomeric 2-methoxy-cinnamic acid. **Coumaroxime**, melting at 131° (B. **19**, 1662), is produced when hydroxylamine acts upon thiocoumarin.

Coumarin Bromide, $C_9H_6O_2Br_2$, melting at 105°, is produced when bromine acts upon coumarin in carbon disulphide solution. Alcoholic potash converts it into α-**brom-coumarin**, $C_6H_4\begin{cases}[1]CH : CBr \\ [2]O — CO\end{cases}$. Boiling alcoholic potash changes both of these bodies into *coumarilic acid* (see this). **Thio-coumarin**, $C_6H_4\begin{cases}[1]CH : CH \\ [2]O — CS\end{cases}$, melting at 101°, consists of golden-yellow needles. It is obtained from coumarin or o-coumaric acid by the action of P_2S_5 (B. **19**, 1661).

3-**Nitro-coumarinic Acid**, $NO_2[3]C_6H_3\begin{cases}[1]CH : CH \\ [2]O — C(OH)_2\end{cases}$ (?), melts when rapidly heated, with the exit of water, at 150°, and passes on gentle warming with water or alcohol into the anhydride 3-*nitro-coumarin*, from which it is obtained upon boiling with soda. It forms long, yellow prisms. The silver salt and methyl iodide yield 3-*nitrocoumarinic dimethyl ether*, $NO_2[3]C_6H_3\begin{cases}[1]CH : CH \\ [2]O — C(OCH_3)_2\end{cases}$ (?) (Constitution, see p. 280).

Coumarin Homologues.—Following method 2, and using propionic, butyric and isovalerianic anhydrides, with their sodium salts, the products are *α-alkyl coumarins*. The *β-alkyl coumarins* are produced from phenols, acetoacetic ester, and sulphuric acid (B. **17**, 2188) by method 4 (p. 279). P_2S_5 converts the α-alkyl coumarins into α-alkyl thio-coumarins (p. 281), which hydroxylamine changes to α-alkyl coumarin oximes

(p. 281) (B. **24**, 3459). The melting points of the latter are given with those of the α-alkyl coumarins:

		M.P.
α-Methyl Coumarin, .	$C_6H_4\left\{\begin{array}{l}CH:C(CH_3)\\O—CO\end{array}\right.$	90° (Th. 122°; Ox. 166°).
β-Methyl Coumarin, .	$C_6H_4\left\{\begin{array}{l}C(CH_3):CH\\O——CO\end{array}\right.$	125°
α-Ethyl Coumarin, .	$C_6H_4\left\{\begin{array}{l}CH:C(C_2H_5)\\O—CO\end{array}\right.$	71° (Th. 93°; Ox. 157°).
p-*β-Dimethyl Coumarin*,	$CH_3.[4]C_6H_3\left\{\begin{array}{l}C(CH_3):CH\\O——CO\end{array}\right.$	148°.
α-Isopropyl Coumarin,	$C_6H_4\left\{\begin{array}{l}CH:C.CH(CH_3)_2\\O—CO\end{array}\right.$	54° (Th. 81°; Ox. 171°).

Dimethylamido-β-methyl Coumarin, melting at 143°, is obtained from dimethylamidophenol and acetoacetic ester (B. **30**, 277).

m-Coumaric Acid, $HO[3]C_6H_4.CH:CH.CO_2H$, melting at 191°, has been formed from m-amido-cinnamic acid and from m-oxybenzaldehyde (B. **15**, 2049, 2297).

Nitro-m-coumaric Acids, see B. **22**, 292.

6-**Amido-m-coumaric Acid** has been obtained electrolytically from o-nitro-cinnamic acid (B. **27**, 1936).

p-Coumaric Acid, $HO[4]C_6H_4.CH:CH.CO_2H$, melting at 206°, is obtained from p-amido-cinnamic acid, and from p-oxybenzaldehyde; also on boiling the extract of aloes with sulphuric acid (Preparation, B. **20**, 2528), and by the decomposition of the glucoside naringine (see this).

Methyl p-coumaric Acid, from anisic aldehyde, melts at 154°. The phenol alkyl-ethers of the coumaric acids yield ethers of unsaturated phenols (see o- and p-vinyl-anisol, p. 266), just as styrolene is obtained from β-bromhydrocinnamic acid, by the action of hydrogen bromide, and then a soda solution, when carbon dioxide is eliminated.

β-p-**Methoxyphenylmethacrylic Acid**, $CH_3O[4]C_6H_4.CH:C(CH_3).COOH$, melting at 154°, is obtained from anisic aldehyde and propionic acid. It breaks down, when heated, into carbon dioxide and anethol (p. 269).

B. **Dioxyphenyl-olefine Carboxylic Acids.**—Caffeïc acid, or 3,4-dioxycinnamic acid, corresponding to protocatechuic acid (p. 227), and umbellic acid, or 2,4-dioxycinnamic acid, are the most important of the known dioxycinnamic acids, because they themselves, or their simple derivatives, occur in plants or appear as decomposition products of vegetable substances, and 3-methyl caffeïc acid, or ferulic acid, can be changed to the valuable vanillin (p. 219).

Caffeïc Acid, β-,3,4-*Dioxyphenylacrylic Acid*, 3,4-*Dioxycinnamic Acid*, and its methyl- and methylene ether-acids, when reduced, become hydrocaffeïc acid and its ether-acids (p. 242). Oxidation yields protocatechuic acid and its ethers. When the acet-derivatives of the two methyl caffeïc acids are oxidized with potassium permanganate the first products are the acet-derivatives of the two methyl-ether protocatechuic aldehydes. The caffeïc acids and their ether-acids can be synthesized from protocatechuic aldehyde and its ethers with the aid of the Perkin reaction (p. 274). When fused with caustic potash caffeïc acid and its ether-acids yield protocatechuic acid and acetic acid:

$$C_6H_3\left\{\begin{array}{l}[1]CH:CH\ CO_2H\\ [3]OH\\ [4]OH\end{array}\right. \qquad C_6H_3\left\{\begin{array}{l}[1]CH:CH.CO_2H\\ [3]OCH_3\\ [4]OH\end{array}\right. \qquad C_6H_3\left\{\begin{array}{l}[1]CH:CH.CO_2H\\ [3]OH\\ [4]OCH_3\end{array}\right.$$

Caffeïc Acid, m.p. 213° — Ferulic Acid, m. p. 169° (yields Vanillin) — Isoferulic Acid, m. p. 228° (yields Isovanillin).

Caffeïc acid is produced when coffee tannic acid is boiled with potassium hydroxide. It occurs in *Cicuta virosa* (B. 17, 1922). Ferric chloride produces a green coloration in its solutions, which sodium carbonate changes to a dark red color.

Ferulic Acid, m-*Methoxy*-p-*oxycinnamic Acid*, occurs in the resin of *Asafœtida*, and has been obtained from vanillin, as well as from m-methoxy-p-nitro-cinnamic acid, the product resulting from the action of nitric acid upon m-methoxycinnamic acid ether (B. 18, R. 682). Its *acet-compound* melts at 196°.

Isoferulic Acid, m-*Oxy*-p-*methoxycinnamic Acid*, *Hesperitinic Acid*, was first obtained from the glucoside hesperidine (see this). Both methyl ethers can also be prepared by a partial methylation of caffeïc acid, when the chief product will be isoferulic acid. Its *acet-derivative* melts at 199°.

Dimethyl Caffeïc Acid, $(CH_3O)_2[3,4]C_6H_3 . CH : CH . CO_2H$, melts at 181° (B. 14, 959).

Piperonyl Acrylic Acid, $(CH_2O_2)[3,4]C_6H_3 . CH : CH . CO_2H$, melts at 232° (B. 13, 757).

Diacetcaffeïc Acid, $(CH_3CO_2)_2[3,4]C_6H_3 . CH : CH . CO_2H$, melts at 190° (B. 11, 686).

a-**Homo-caffeïc Acid,** 3,4-Dioxy-*a*-methyl Cinnamic Acid, melts at 193°. Its monomethyl ether-acid, **Homoferulic Acid,** $(CH_3O)(OH)[3,4]C_6H_3 . CH : C(CH_3) . COOH$, melting at 168°, yields isoeugenol when it is heated with lime (p. 270) (B. 15, 2063).

a-**Hydropiperic Acid,** $(CH_2O_2)[3,4]C_6H_3CH_2 . CH : CH . CH_2 . CO_2H$, melting at 78°, is formed when sodium amalgam acts upon piperic acid. When boiled with caustic soda it changes to *β*-**Hydropiperic Acid,** $(CH_2O_2)[3,4]C_6H_3 . CH_2 . CH_2 . CH : CH . CO_2H$, melting at 131°. Sodium amalgam converts the *β*-acid into *piperhydronic acid*, $(CH_2O_2)[3,4]C_6H_3[CH_2]_4CO_2H$, melting at 98°.

Umbellic Acid, 2,4-*Dioxycinnamic Acid*, $(HO)_2[2,4]C_6H_3 . CH : CH . CO_2H$, decomposes about 240°. It is produced on boiling—

Umbelliferone, 4-*Oxycoumarin*, $HO[4]C_6H_3\begin{cases}[1]CH : CH \\ [2]O—CO\end{cases}$, melting at 240°, with caustic soda. It is found in the bark of *Daphne mezereum*, and is obtained by distilling different resins, such as galbanum and asafœtida. It is obtained synthetically from *β*-resorcyl aldehyde by method 2; and also by the condensation of resorcinol with malic acid according to method 3. It has an odor resembling that of coumarin, and behaves similarly with caustic potash. Its alkyl ethers show isomeric phenomena analogous to those developed under o-coumaric acid and coumarin (p. 281) (B. 19, 1778).

β-**Methyl Umbelliferone,** 4-*Oxy*-*β*-*methylcoumarin*, *Resocyanine*,

$HO[4]C_6H_3\begin{cases}[1]C(CH_3) : CH \\ [2]O—CO\end{cases}$, melting at 185°, is formed when sulphuric acid acts upon resorcinol and acetoacetic ester or acetylcyanacetic ester (B. 26, R. 314). See resacetophenone p. 221. *a*-,*β*-**Dimethyl Umbelliferone** melts at 256° (B. 16, 2127).

The corresponding bodies have been prepared from orcinol according to methods 3 and 4 (p. 279) (B. 17, 1649, 2188).

3-**Oxycoumarin,** melting at 280–285° with decomposition, and 5-**Oxycoumarin,** melting at 249°, are produced when pyrocatechol and hydroquinone are treated with malic acid and sulphuric acid (B. 18, R. 333).

C. **Trioxycinnamic Acids.**—Inner anhydrides, *δ*-lactones of trioxycinnamic acids, are **Daphnetin,** 3,4-*Dioxycoumarin*, melting at 255°, and **Æsculetin,** 4,5-*Dioxycoumarin*, the aromatic decomposition products of the isomeric glucosides daphnin and æsculin. Æsculetinic and daphnetic acids are the trioxycinnamic acids corresponding to these dioxycoumarins. They are only known as ether-acids and ether-esters. Potassium permanganate oxidizes the triethyl ethers to triethoxybenzoic acids, which become triethoxybenzenes through the loss of carbon dioxide (B. 15, 2082; 17, 1086; 20, 1119).

D. **Tetra-oxycinnamic Acids.**—**Fraxetin,** melting at 227°, the aromatic decomposition product of the glucoside of fraxin (see this), contains the monomethyl ether of a trioxycoumarin. Isomerides of fraxetin have been prepared synthetically (B. 27, R. 130; 29, R. 293).

8. Phenylacetylene Carboxylic Acids.

Phenyl-propiolic acid, corresponding to propiolic acid, is important because of its intimate connection with indigo and isatine.

Phenyl-propiolic Acid, $C_6H_5.C : C.CO_2H$, melting at 136°, is obtained by boiling *α*- and *β*-brom-cinnamic acids with alcoholic potash, by acting upon sodium phenyl-acetylene with carbon dioxide (1870, Glaser, A. **154**, 140), and when the latter and sodium act upon *ω*-brom-styrolene. It is prepared by boiling the dibromide of ethyl cinnamate (p. 255) with alcoholic potash. When heated to 120° with water it decomposes into carbon dioxide and phenyl acetylene. It yields hydro-cinnamic acid with sodium amalgam. Zinc-dust and glacial acetic acid, or sodium and methyl alcohol, convert it into cinnamic acid (B. **22**, 1181).

Hydrogen chloride and bromide convert it into *β*-haloid- and allo-*β*-haloid cinnamic acids (p. 276). It combines with the halogens to phenyl-dihaloid acrylic acids, with hydrazine and phenylhydrazine to 3 phenyl-pyrazolon (see this) and 1,3-diphenylpyrazolon (B. **27**, 783), and with sodium malonic ester to a tricarboxylic ester, which splits off carbon dioxide and becomes phenylglutaconic acid (p. 289) (B. **27**, R. 163).

Ethyl Phenylpropiolic Ester, $C_6H_5.C : C.CO_2C_2H_5$, boiling at 260–270°, readily absorbs water and becomes benzoyl acetic ester (p. 259). Its *chloride* boils at 131° (25 mm.). Its *amide* melts at 102° (B. **25**, 3537; **29**, R. 795).

o-**Nitro-phenyl Propiolic Acid** decomposes at 156°. It is obtained when alcoholic potash acts upon the dibromide of o-nitro-cinnamic acid (Baeyer, A. **212**, 140). When boiled with water it decomposes into carbon dioxide and o-nitro-phenyl acetylene. When boiled with alkalies it yields isatin.

It dissolves in concentrated sulphuric acid, with conversion into the isomeric *isatogenic acid*, which at once forms carbon dioxide and isatin. Its *silver salt* explodes with great violence when it is heated.

If digested with alkaline reducing agents (grape-sugar and potassium hydroxide, ferrous sulphate, hydrogen sulphide, potassium xanthate) *it readily changes to indigo blue* (Baeyer, 1880; B. **13**, 2259).

Despite its comparatively high price, therefore, nitrophenyl propiolic acid is prepared technically, and serves as a substitute for natural indigo, especially in calico printing.

The *ethyl ester* of the acid is obtained by conducting hydrochloric acid gas into the mixture of the acid and alcohol. It melts at 60–61°. When it is dissolved in sulphuric acid it changes to the isomeric isatogenic ester. Ammonium sulphide reduces it to the indoxylic ester (B. **14**, 1741):

$$C_6H_4\begin{cases}[1]CO.C.CO_2C_2H_5\\ [2]N\angle O\end{cases} \leftarrow C_6H_4\begin{cases}[1]C : C.CO_2C_2H_5\\ [2]NO_2\end{cases} \rightarrow C_6H_4\begin{cases}[1]C(OH)\diagdown\\ [2]N = \!=\!\diagup\end{cases}\!\!C.CO_2C_2H_5$$

Isatogenic Ester — o-Nitrophenylpropiolic Ethyl Ester — Indoxylic Ester.

p-*Nitro-phenyl Propiolic Acid*, melting at 198°, is formed from the p-nitro-cinnamic ester after the same manner as the ortho-acid. When boiled with water it breaks up into carbon dioxide and p-nitrophenylacetylene. It yields p-nitroacetophenone if digested at 100° with sulphuric acid.

The *ethyl ester*, melting at 126°, when digested with sulphuric acid at 35°, forms p-nitrobenzoyl acetic acid (p. 260).

o-Amido-phenyl Propiolic Acid melts at 129° with decomposition into CO_2 and o-amido-phenyl acetylene (p. 268). It is obtained by reducing o-nitrophenyl propiolic acid with ferrous sulphate and ammonia (B. **16**, 679). It separates as a yellow, crystalline powder. When boiled with water it yields o-amido-acetophenone (p. 190).

γ-Chlorcarbostyril results when the acid is boiled with hydrochloric acid, and **γ-oxycarbostyril** upon heating it with sulphuric acid (B. **15**, 2147):

$$C_6H_4\left\{\begin{array}{l}CCl:CH\diagdown\\ N{=\!=\!=\!=}\diagup\end{array}\right.\!\!C.OH \xleftarrow[-H_2O]{+HCl} C_6H_4\left\{\begin{array}{l}[1]C\equiv C.CO_2H\\ [2]NH_2\end{array}\right. \longrightarrow C_6H_4\left\{\begin{array}{l}C(OH):CH\diagdown\\ N{=\!=\!=\!=}\diagup\end{array}\right.\!\!COH.$$

Sodium nitrite converts the hydrochloride into the diazo-chloride, which at 70° yields cinnoline-oxy-carboxylic acid.

m-Methylphenyl Propiolic Acid, $CH_3[3]C_6H_4C:C.CO_2H$, melts at 109° (B. **20**, 1215).

9. **Phenyldiolefine Carboxylic Acids** have been prepared from cinnamic aldehyde by means of the Perkin reaction (p. 274). **Cinnamenyl Acrylic Acid,** $C_6H_5.CH:CH.CH:CH.CO_2H$, melts at 165°. The *nitrile*, boiling at 285°, is obtained from cinnamenyl cyanacrylic acid (p. 289). The o- and p- nitro-acids, melting at 217° and 271°, were obtained from o- and p-nitrocinnamenyl acetone (p. 273) by the action of NaClO (A. **253**, 356). The o-*amido-acid* melts with decomposition at 176° (B. **18**, 2332). *Cinnamenyl Crotonic Acid* and *Cinnamenyl Angelic Acid* melt at 157° and 126°.

Piperic Acid, 3,4-Methylenedioxy-cinnamenyl Acrylic Acid, $(CH_2O_2)[3,4]C_6H_3.CH:CH.CH:CH.CO_2H$, melting at 217°, is produced, together with piperidine, when piperine is boiled with alcoholic potassium hydroxide. It can be synthesized by aid of the Perkin reaction from piperonylacroleïn, and from piperonylene malonic acid (p. 289) (B. **28**, 1190). Sodium amalgam converts it into two isomeric **hydropiperic acids,** α and β. It combines with four atoms of bromine. It is oxidized in dilute solution by potassium permanganate, at 0°, to piperonal and racemic acid (B. **23**, 2372). When fused with potassium hydroxide it breaks down into acetic, oxalic, and protocatechuic acids. Its chloride and piperidine form piperine (see this).

History.—Fittig and Mielck (1874) determined the constitution of piperic acid. Ladenburg and Scholtz (1894) effected its synthesis (B. **27**, 2958).

α-Methyl- and α-Ethyl Piperic Acids, melting at 208° and 179°, were synthesized just like piperic acid (B. **28**, 1187).

IV. COMPOUNDS WHICH MAY BE VIEWED AS OXIDATION PRODUCTS OF MONO-NUCLEUS, AROMATIC POLYALCOHOLS WITH UNSATURATED SIDE-CHAINS.

The domain of the aromatic polyalcohols having unsaturated side-chains has been even less completely and even more irregularly developed than that of the polyhydric, aromatic paraffin alcohols and their oxidation products. At present the alcohols and aldehydes are wholly lacking; from them the carboxylic acids and their derivatives belonging here can be theoretically deduced. Consequently the material in this section will not be sharply differentiated, although in the main the classification is the same as that observed with the oxidation products of the aromatic polyparaffin alcohols (pp. 232–266).

1. *Phenylene Oxyolefine Carboxylic Acids.*—*Methylene phthalide* and *isocoumarin* are inner anhydrides or lactones of the possible o-vinyl alcohol benzoic acids, not known in a free state. Coumarin is isomeric with them.

Methylene Phthalide, $C_6H_4\left\{\begin{array}{l}[1]C=CH_2\\ \quad\ \ \diagdown\\ [2]COO\end{array}\right.$, melting at 59°, is formed in the distillation of phthalyl acetic acid (p. 290). Its *dibromide* melts at 98°. *Monobrom-methyl-*

ene phthalide, $C_6H_4\begin{cases}[1]C=CHBr\\ \quad\diagdown\\ [2]CO.O\end{cases}$, is produced by the action of bromine upon o-acetophenone-carboxylic acid. *Dichlor-methylene phthalide*, $C_6H_4\begin{cases}[1]C=CCl_2\\ \quad\diagdown\\ [2]COO\end{cases}$, melts at 128°. It is formed, together with *Tetrachlormethyl phthalide*, $C_6H_4\begin{cases}CCl.CCl_3\\ \quad\diagdown\\ COO\end{cases}$, melting at 93°, upon conducting chlorine into a mixture of glacial acetic acid and phthalyl chlor-acetic acid (A. **255**, 383; **268**, 294). Derivatives of *methylene phthalimidine*, $C_6H_4\begin{cases}[1]C=CH_2\\ \quad ——\\ [2]CO.NR\end{cases}$, have been prepared by the action of amines and amin-acids upon o-acetophenone carboxylic acid (B. **29**, 2518). *Ethidene phthalide*, $C_6H_4\begin{cases}[1]C=CH.CH_3\\ \quad\diagdown\\ [2]COO\end{cases}$, melts at 64° (B. **19**, 838).

Propidene- and *Isobutylidene Phthalides*, boiling at 170° (12 mm.) and melting at 97°, are obtained by condensing phthalic anhydride with the sodium salts and anhydrides of propionic, butyric, and isovaleric acids. Water and carbon dioxide are eliminated (B. **29**, 1436).

Isocoumarin, $C_6H_4\begin{cases}[1]CH=CH\\ \qquad\quad\ |\\ [2]CO-O\end{cases}$, melting at 47° and boiling at 285°, is formed in the distillation of silver isocoumarin-carboxylate. It readily volatilizes with steam. When digested with soda it becomes—

Anhydro-o-oxyvinyl Benzoic Acid, $O(CH:CH[2]C_6H_4.CO_2H)_2$, melting at 183°. When this body is heated with hydrochloric acid to 100° the *anhydride*, $O(CH:CH[2]C_6H_4.CO)_2O$, melting at 234°, results. The *imide*, $O(CH:CH[2]C_6H_4CO)_2NH$, melting at 285°, is produced when alcoholic ammonia acts upon the anhydride at 170° (B. **27**, 207).

Isocarbostyril, $C_6H_4\begin{cases}[1]CH=CH\\ \qquad\quad\ |\\ [2]CO-NH\end{cases}$, melting at 208°, is isomeric with carbostyril (p. 277), the lactam corresponding to isocoumarin. It is formed when isocoumarin is heated to 130° with alcoholic ammonia, and upon heating isocarbostyril-carboxylic acid (p. 290) or its silver salt. It yields isoquinoline when distilled with zinc-dust (B. **27**, 208).

3-Methyl-isocoumarin, $C_6H_4\begin{cases}[1]CH=C.CH_3\\ \qquad\quad\ |\\ [2]CO-O\end{cases}$, melting at 118°, is formed when *ψ-diacetylcyanbenzylcyanide*, $C_6H_4\begin{cases}[1]C=C(O_2CCH_3)CH_3\\ \quad\diagdown\\ [2]CN\ CN\end{cases}$, melting at 135°, is heated to 180° with hydrochloric acid. This latter body results from the action of sodium acetate and acetic anhydride upon o-cyanbenzyl cyanide (B. **27**, 831). Similarly o-cyanbenzyl cyanide furnishes an additional series of homologues of isocoumarin, all of which are characterized by their ready transposition into isocarbostyrils (see B. **29**, 2543, etc.).

Ammonia converts 3-methyl-isocoumarin into the corresponding *3-Methylisocarbostyril*, melting at 211° (B. **25**, 3563).

Bergapten, $\left.\begin{matrix}CH=CH\\ |\!\!——O\end{matrix}\right\}C_6H(OCH_3)\begin{cases}CH=CH\\ |\qquad\ |\\ O——CO\end{cases}$ (?), melting at 188°, appears to be a derivative of oxyvinylcoumarin. It separates, on standing, from red bergamot oil, which is obtained by pressing out the fresh hulls of *Citrus Bergamia Risso* (B. **26**, R. 234).

2. *Phenylene Aldehydo-carboxylic Acids.*—**p-Aldehydo-cinnamic Acid**, $CHO[4]C_6H_4.CH:CH.CO_2H$, melting at 247°, is obtained from terephthal-aldehyde by the Perkin reaction (p. 274) (A. **231**, 375).

3. *Phenylene Dicarboxylic Acids.*—**o-Cinnamyl Carboxylic Acid**, $CO_2H[2]C_6H_4$.-

$CH:CH.CO_2H$, melts at 174°, and reverts again to phthalidacetic acid. It is produced when phthalidacetic acid is digested with alkalies and by carefully oxidizing β-naphthol with potassium permanganate (B. **21**, R. 654). More energetic oxidation produces carbophenyl glyoxylic acid (p. 265).

o-Cyan-cinnamic Acid, $CN[2]C_6H_4CH:CH.CO_2H$, melting at 252°, is produced when sodium acetate and acetic anhydride act upon o-cyanbenzal chloride, and also from o-amido-cinnamic acid (B. **24**, 2574; **27**, R. 262).

p-Cinnamyl Carboxylic Acid is obtained from terephthal-aldehydic acid and sodium acetate. It is an insoluble, infusible powder (A. **231**, 369).

o-Phenylenediacrylic Acid, $C_6H_4[1,2](CH:CH.CO_2H)_2$, melts above 300°. It is produced when alcoholic potash acts upon o-xylylene dichlordimalonic ester (B. **19**, 435). **p-Phenylenediacrylic Acid** is obtained from p-aldehydo-cinnamic ester with sodium acetate and acetic anhydride (A. **231**, 377), and from p-xylylene dibromdimalonic ester.

4. *Phenylolefine Ketols.*—**Oxymethylene Acetophenone**, $C_6H_5.CO.CH:CH.OH$, when separated from its sodium compound, is a very unstable oil. Its sodium derivative is formed when sodium ethylate acts upon formic ester and acetophenone. Formerly, oxymethylene acetophenone was considered to be *benzoyl acetaldehyde* (p. 250). Constitution of the oxymethylene compounds—see 1, 319. Phenylhydrazine converts it into diphenylpyrazole (see this); hydroxylamine unites with it to form benzoylacetaldoxime (p. 250).

5, 6. *Phenyl-oxyolefine and Diolefine Carboxylic Acids.*—**Oxymethylene-phenyl-acetic Ester**, $C_6H_5C(CO_2C_2H_5):CHOH$—see formyl phenylacetic ester, p. 256.

β-Ethoxycinnamic Ester, $C_6H_5C(OC_2H_5):CH.CO_2C_2H_5$, boiling at 171–173°, is obtained from benzoyl acetic ester and orthoformic ester. The corresponding acid melts at 162° with evolution of carbon dioxide and the formation of β-phenylvinylethyl ether (p. 271) (B. **29**, 1005).

Phenyl-α-oxy-crotonic Acid, $C_6H_5CH:CH.CH(OH)COOH$, melting at 137°, is prepared by saponifying its nitrile, *cinnamyl-aldehyde cyanhydrin*, melting at 80°, with cold concentrated hydrochloric acid. On boiling with hydrochloric acid the acid is readily rearranged to benzoyl propionic acid (p. 261) (B. **29**, 2582).

β-Benzylangelic Lactone, $C_6H_5.CH_2C\langle{}^{CH_2.COO}_{C.CH_3}$, is obtained in the distillation of benzyl-lævulinic acid (p. 261).

δ-Oxycinnamylidene Acetic Acid.

Its lactone is *phenylcoumalin*, $C_6H_5.C:CH.CH:CH.CO$ (ring closed through O), melting at 68°, and found in coto-bark (B. **29**, 2659; R. 1116).

7, 8. *Phenyl-olefine- and diolefine-α-keto-carboxylic acids* result from the condensation of aromatic aldehydes with pyroracemic acid.

Cinnamyl Formic Acid, $C_6H_5.CH:CH.CO.CO_2H$, a bright yellow gummy mass, is obtained from its nitrile, *cinnamyl cyanide*, $C_6H_5.CH:CH.CO.CN$ (B. **14**, 2472), melting at 140°.

The *ortho-nitro derivative* is similarly formed from o-nitrobenzaldehyde and pyroracemic acid. It melts at 135°, and is changed by alkalies, even in the cold, with elimination of oxalic acid, into indigo.

3,4-Methylene-dioxycinnamyl Formic Acid, $(CH_2O_2)[3,4]C_6H_3.CH:CH.CO.CO_2H$, melting at 148–150°, and **piperonylene-pyroracemic acid**, $(CH_2O_2)[3,4]C_6H_3CH:CH.CH.CH.CO.CO_2H$, melting at 165–167°, are formed from piperonal and piperonyl acroleïn (p. 272).

9. *Phenyl-olefine-β-keton Carboxylic Acids* result from the condensation of acetoacetic ester and aromatic aldehydes with hydrochloric acid gas, or, better, primary or secondary amines in the cold (B. **29**, 172). **Benzal Acetoacetic Ester**, $C_6H_5.CH:C\langle{}^{CO_2C_2H_5}_{COCH_3}$, melting at 59° and boiling at 181° (17 mm.) (A. **281**, 63). The *m-nitro-ester* melts at 112° (B. **26**, R. 448). **Allyl Benzoyl Acetic Ester**, $C_6H_5.CO.CH.\langle{}^{CO_2C_2H_5}_{CH_2.CH:CH_2}$, melts at 122° (B. **16**, 2132).

Benzal Diethyl Acetoacetic Ester, $C_6H_5.CH:CH.COC(C_2H_5)_2.CO_2C_2H_5$, melts at 101°.

10. *Phenyl-olefine-γ-ketone Carboxylic Acids* result by the condensation (1) of aldehydes and ketone-carboxylic acids with acids or alkalies; (2) of olefine dicarboxylic anhydrides—*e.g.*, maleïc acid anhydride, citraconic anhydride, and benzenes with aluminium chloride.

β-**Benzoyl Acrylic Acid,** $C_6H_5.CO.CH:CH.CO_2H$, melts at 96° when anhydrous. It results from the action of sulphuric acid upon maleïc anhydride (see above), as well as from phenyl-γ-keto-α-oxybutyric acid (p. 261). **Trichlorethidene Acetophenone,** $C_6H_5.CO.CH:CH.CCl_3$, melting at 102°, is produced when sulphuric acid acts upon chloral-acetophenone (p. 261). β-**Benzoyl Crotonic Acid,** $C_6H_5.CO.C(CH_3):CH.CO_2H$, melting at 113°, is obtained from citraconic anhydride (B. **15**, 891).

β-**Benzal-lævulinic Acid,** $C_6H_5.CH:C<\begin{matrix}CO.CH_3\\CH_2.CO_2H\end{matrix}$, melting at 125°, is produced by the condensation of benzaldehyde and lævulinic acid in *acid solution*. It parts with water upon distillation and forms 3-aceto-1-naphthol. Phenylitaconic acid is formed by its oxidation, and β-benzyl-lævulinic acid by its reduction. Hydroxylamine produces the neutral *lactoxime*, *Benzal lævoxime*, $C_6H_5.CH:C<\begin{matrix}CH_2CO\\ \quad C:N.O\end{matrix}$ / CH_3, melting at 94°.

When benzaldehyde and lævulinic acid condense in *alkaline solution* the product is—

δ-**Benzal-lævulinic Acid,** $C_6H_5CH:CH.CO.C_2H_4.CO_2H$, melting at 120°. It yields *benzal-angelic lactone*, melting at 90° (B. **24**, 3202), upon distillation.

11, 12. *Phenylolefine-* and *diolefine Dicarboxylic Acids.*—**Benzal Malonic Acid,** $C_6H_5.CH:C(CO_2H)_2$, melts with production of cinnamic acid and allocinnamic acid (p. 274). It is formed in the condensation of benzaldehyde, malonic acid, and glacial acetic acid. Its *ethyl ester*, boiling at 198° (13 mm.), is obtained from benzaldehyde, malonic ester, and hydrochloric acid. It adds to itself more readily than the free acid. Aniline as well as phenylhydrazine converts the methyl ester into β-**Anilido-** and β-**Phenylhydrazido-benzyl-malonic Methyl Ester,** melting at 117° and 94° (B. **29**, 813). When substituted benzaldehydes are used, substituted benzal-malonic acids result —*e. g.*, **nitrobenzal malonic acid,** which is reduced by ferrous sulphate and ammonia to β-carbostyril carboxylic acid (B. **21**, R. 253).

α-**Cyan-cinnamic Acid,** *Half-nitrile of Benzal Malonic Acid,*

$C_6H_5.CH:C<\begin{matrix}CO_2H\\CN\end{matrix}$, melting at 180°, is obtained by the action of cyan-acetic acid in the heat upon benzaldehyde, or when it is boiled with cyanacetyl chloride. When heated it passes into the nitrile of cinnamic acid (p. 274). The *methyl* and *ethyl esters* melt at 70° and 50°. A large number of half-nitriles of unsaturated, aromatic malonic acids of related constitution have been obtained by the union of readily accessible, aromatic aldehydes with cyan-acetic acid (B. **27**, R. 262). *Nitrile Acid Amide*, *dinitrile*, and *diamide* of benzal malonic acid, melting at 123°, 87°, and 190°, have also been synthesized by the condensation of benzaldehyde with cyanacetamide, malonitrile, and malonamide (B. **28**, 2251).

β-**Carbostyril Carboxylic Acid,** $C_6H_4\begin{cases}[1]CH:C.CO_2H\\ [2]NH.CO\end{cases}$, is formed from o-amidobenzaldehyde upon heating it with malonic acid to 120°, and also from o-nitrobenzal malonic acid (B. **21**, R. 353). Its silver salt, when heated, yields carbostyril.

Coumarin Carboxylic Acid, $C_6H_4\begin{cases}[1]CH:C.CO_2H\\ [2]O\text{——}CO\end{cases}$, melting at 187°, breaks down at 290° into carbon dioxide and coumarin (p. 281). It is obtained from salicylaldehyde, malonic acid, and glacial acetic acid, as well as from—

Cyan-coumarin, $C_6H_4\begin{cases}[1]CH:C.CN\\ [2]O\text{——}CO\end{cases}$, melting at 182°. This latter body may be prepared by the action of dilute sulphuric acid upon **o-oxybenzaldicyanacetic ester,** $HO[2]C_6H_4CH[CH(CN)CO_2C_2H_5]_2 + \frac{1}{2}H_2O$, melting at 140°. This is a condensation product of salicylaldehyde and cyanacetic ester (B. **27**, R. 576).

Cinnamenyl Malonic Acid, *Phenyl-butine Dicarboxylic Acid*, $C_6H_5 . CH : CH . CH : C(CO_2H)_2$, melts at 208° (B. 19, R. 350). **Cinnamenyl Cyanacrylic Acid,** $C_6H_5 . CH : CH . CH : C(CN)CO_2H$, melts at 212°.

Piperonylene Malonic Acid, $(CH_2O_2)[3,4]C_6H_3 . CH : CH . CH : C(CO_2H)_2$, melts at 205° with decomposition into CO_2 and piperic acid (p. 285) (B. 28, 1190). **Phenyl Allyl Malonic Acid,** $C_6H_5C(CH_2 . CH : CH_2)(COOH)_2$, melts with decomposition at 145°. Its ester is formed when allyl iodide acts upon phenyl malonic ester (B. 29, 2600).

Phenyl Maleïc Acid, $\begin{array}{l} CH . CO_2H \\ \| \\ C_6H_5 . C . CO_2H \end{array}$, changes below 100° into its ***anhydride***, melting at 119°, which is produced when bromine and PBr_3 act upon phenylsuccinic acid, and the reaction product is treated with water. Phenylmalic acid is formed simultaneously (B. 23, R. 573).

Phenyl Itaconic Acid, $\begin{array}{l} C_6H_5 . CH : C . CO_2H \\ \qquad\qquad\quad | \\ \qquad\qquad CH_2 . CO_2H \end{array}$, melting at 172°, is formed (1) from succinic ester, benzaldehyde, and sodium ethylate; (2) from phenyl paraconic ester and sodium ethylate. When fused, particularly under reduced pressure, it separates into water and its *anhydride*, melting at 163–166°, which in every fusion changes in a slight degree to isomeric *phenylcitraconic anhydride*, melting at 60°. Water changes the latter to *phenylcitraconic acid*, melting at 103–106°. If phenylcitraconic acid in chloroform solution, to which a little bromine is added, be exposed to sunlight, it becomes *phenylmesaconic acid*, melting at 210°.

The conversion of phenylitaconic acid in chloroform solution, to which a few drops of a dilute bromine solution have been added, into *phenylaticonic acid*, melting at 148° (B. 26, 40, 2082; 27, 2405) (1, 465), when exposed to sunlight, is certainly very remarkable.

Coumarin-propionic Acid, $C_6H_4\left\{\begin{array}{l} [1]CH = C . CH(CH_3)CO_2H \\ \qquad\qquad\quad | \\ [2]O \text{———} CO \end{array}\right.$, melting at 171°, is formed, together with o-oxyphenyl methylisocrotonic **acid,** from salicylaldehyde, sodium pyroracemate, and acetic anhydride. It passes into α-ethyl coumarin when it is distilled (A. 255, 285).

Methyl Phenyl Itaconic Acid, $C_6H_5C(CH_3) = C(CO_2H)CH_2 . CO_2H$, melts with decomposition at 161–163°. It is obtained from succinic ethyl ester, acetophenone, and sodium ethylate in ether (A. 282, 288).

Phenyl Glutaconic Acid, $C_6H_5 . C(CH_2 . COOH) : CH . COOH$, melting at 154°, has been obtained from the condensation product formed in the union of phenylpropiolic ester with sodium malonic ester (B. 27, R. 163).

Benzal Glutaric Acid, $C_6H_5 . CH : C(CO_2H)CH_2 . CH_2 . COOH$ (A. 282, 338).

Benzyl Glutaconic Ester, $C_6H_5 . CH_2 . CH(COOH)CH : CH . COOH$, melts at 145° (A. 222, 261). Its *ethyl ester*, boiling at 203° (10 mm.), when treated with ammonia at 100°, forms *dihydroxybenzyl pyridine*, melting at 184° (B. 26, R. 318). (Compare constitution of pyridine.)

13. **Phenylene Oxyolefine Dicarboxylic Acids.**—Phthalyl acetic acid and isocoumarin carboxylic acid have the same relation to each other that methylene phthalide sustains to isocoumarin. Phthalyl acetic acid and its homologues have been obtained by applying the Perkin reaction to phthalic anhydride:

Phthalyl Acetic Acid, $C_6H_5\left\{\begin{array}{l} C = CH . CO_2H \\ \quad \diagdown \\ COO \end{array}\right.$, melts with decomposition above 260°. When distilled under greatly diminished pressure it breaks down into carbon dioxide and methylene phthalide (p. 285). Salts of benzoylaceto-carboxylic acid (p. 263) are obtained by dissolving it in alkalies. When it is heated with water to 200° it breaks down into carbon dioxide and o-acetylbenzoic acid. When heated with ammonia it forms *Phthalimide Acetic Acid*. The alkylamines react analogously.

Sodium ethylate converts phthalylacetic acid into the sodium salt of diketohydrindene carboxylic acid (see this) (B. 26, 953).

Isocoumarin Carboxylic Acid, $C_6H_4\begin{cases}[1]CH = C - CO_2H \\ [2]CO - O\end{cases}$, melting at 237°, is formed when o-carbophenyl glyceric acid lactone (p. 265) is heated to 160° with hydrochloric acid. See isocoumarin. Ammonia converts it quite readily into *isocarbostyril carboxylic acid,* $C_6H_4\begin{cases}[1]CH = C.CO_2H \\ [2]CO - NH\end{cases}$, melting at 320° (B. 25, 1138). Boiling caustic potash decomposes it into o-toluic acid and oxalic acid (B. 28, R. 770).

14. *Phenylene Oxyolefine Tricarboxylic Acids.* — **Phthalyl Malonic Ester,** $C_6H_4\begin{cases}[1]C = C(CO_2C_2H_5)_2 \\ \quad\diagdown \\ [2]COO\end{cases}$, melting at 74°, is formed, together with phthalyl dimalonic ester (p. 265), from phthalyl chloride and sodium malonic ester (A. 242, 46). **Phthalyl Cyanacetic Ester,** $C_6H_4\begin{cases}[1]C = C<^{CO_2C_2H_5}_{CN} \\ \quad\diagdown \\ [2]COO\end{cases}$, melting at 175°, is made from phthalyl chloride and sodium cyanacetic ester (B. 26, R. 370).

B. HYDROAROMATIC SUBSTANCES WITH SINGLE-NUCLEUS, HYDROBENZENE DERIVATIVES.

It was shown in the introduction to the carbocyclic compounds that the treatment of the hydroaromatic derivatives presupposed a knowledge of the aromatic bodies (p. 18). Indeed, numerous reactions which led to the hydroaromatic compounds, especially the additions, were described in connection with the aromatic substances. Many bodies discussed under the aromatic derivatives—*e. g.*, the quinones—are rather to be viewed as derived from the hydroaromatic hydrocarbons. And reactions were also learned in the discussion of the fatty bodies which will again be encountered, and through which mono-nucleus, hydroaromatic substances are produced. The *terpenes* and *camphor* will be included in the hydroaromatic derivatives.

1. HYDROAROMATIC HYDROCARBONS.

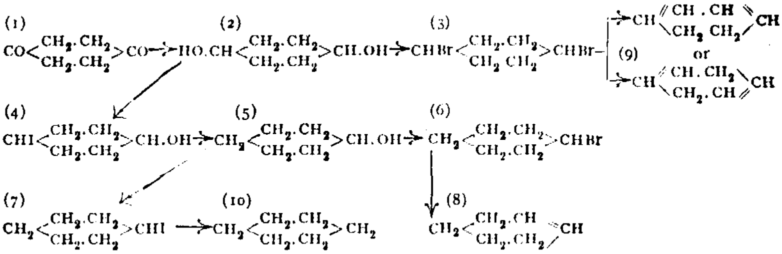
Hexahydrobenzene is the parent hydrocarbon of the hydroaromatic substances. Tetra- and di-hydrobenzene bear the same relation to it that an olefine and a diolefine show to the paraffin, having the same number of carbon atoms.

The hexahydrobenzenes, which are isomerides of olefines with a like number of carbon atoms, resemble the paraffins in chemical deportment; they belong to the cycloparaffins (compare 1, 89; 11, 17), while the tetrahydrobenzenes belong to the cyclo-olefines, the dihydrobenzenes to the cyclodiolefines, and benzene is the simplest imaginable cyclotriolefine, if we accept the formula proposed for it by Aug. Kekulé.

Berthelot (1867) first effected the reduction of benzene to hexahydrobenzene. It was obtained pure by Baeyer (1894) in the course of an investigation in which he demonstrated how the simplest representatives of the hydroaromatic bodies—hexahydrobenzene, tetrahydrobenzene, and dihydrobenzene—could be prepared from p-diketohexamethyl-

ene, a decomposition product of succino succinic ester (p. 305). Before beginning a detailed description of the hydroaromatic hydrocarbons it may be well to briefly present the steps of this research in a diagram. The inclosed numbers following the names refer to the formulas of the diagram.

p-Diketohexamethylene (1) yields quinite (2) by reduction, which hydrogen bromide changes to p-dibromhexamethylene, and hydrogen iodide into the monoiodhydrin (4) of quinite, along with p-diiodhexamethylene. Quinite monoiodhydrin, when reduced, yields oxyhexamethylene (5). Hydrogen bromide and iodide convert oxyhexamethylene (6) into brom- and iod-hexamethylene (6, 7). When p-dibromhexamethylene and monobromhexamethylene are heated with quinoline the latter yields *tetrahydrobenzene* (8), and the former dihydrobenzene (9); whereas mono-iod-hexamethylene is reduced by zinc-dust and glacial acetic acid to *hexahydrobenzene* (10):



Compare the tetrahydrobenzenes (p. 293) for additional methods for the preparation of hydrobenzene derivatives.

The following values (V) and differences (D) were observed by Stohmann in determining the heats of combustion and the boiling points of benzene, the three hydrobenzenes, and hexane:

				Approximately
C_6H_6 (V)	= 779.8	D = 68.2 Cal.	B. P. 80.4°	D = + 5°
C_6H_8 "	= 848.0	" = 44.0 "	" 84–86°	" = — 2°
C_6H_{10} "	= 892.0	" = 41.2 "	" 82–84°	" = — 3°
C_6H_{12} "	= 933.2	" = 58.0 "	" 79–79.5°	" = —10°.
C_6H_{14} "	= 991.2		" 69°	

The differences calculated from these numbers would have to be equal if the changes were of like character. The magnitude of these differences expresses, therefore, the magnitude of the changes involved in the reduction (A. 278, 115). Consult Brühl, B. 27, 1065, upon the value of molecular refraction in the determination of structural differences.

1 a. HEXAHYDROBENZENES, NAPHTHENES [CYCLOHEXANES].

Hydroaromatic hydrocarbons constitute the chief portion of Caucasian petroleum (1, 88) (Beilstein and Kurbatow, B. 13, 1818). Markownikow has, therefore, designated them naphthenes. Hexahydrobenzenes have also been discovered in the tar from bituminous coal and in that from certain shales, as well as in the *resin-oils* obtained from the distillation of colophonium. They have been made artificially by reducing aromatic hydrocarbons with hydriodic acid at high temperatures. Hexahydrobenzene resists decomposition by means of hydrogen very strongly

(A. **278**, 88). The hexahydrobenzenes are more easily obtained by reducing their halogen substitution products.

When hydriodic acid is used as a reducing agent, under certain circumstances alkylpentamethylenes appear to form by a process of isomerization; these are isomeric with the hexamethylenes. Thus, methylpentamethylene is formed together with hexamethylene (B. **30**, 1214).

The hexahydrobenzenes are distinguished from the olefines isomeric with them by their higher specific gravity and their inability to take up bromine. Like the paraffins, they are first changed by chlorine into mono-chlor substitution products, from which esters of monacid alcohols, amines, and tetrahydrobenzenes can be prepared by well-known methods. Substituted aromatic hydrocarbons are obtained from the hexahydrobenzenes by the action of bromine and aluminium bromide, as well as by the action (although with difficulty) of nitric acid and sulphuric acid. However, nitrohydrobenzenes have been obtained by the use of dilute nitric acid (B. **25**, R. 107; **28**, 577).

Hexahydrobenzene . . .	boils at 79°;	sp. gr.	0.7473 (0°)
Hexahydrotoluene . . .	" " 100°;	" "	0.7778 (0°)
Hexahydro-m-xylene . .	" " 118°;	" "	0.7814 (0°)
Hexahydrocumene . . .	" " 148°;	" "	0.7870 (20°)
Hexahydromesitylene .	" " 137°;	" "	——
1,3,4-**Hexahydropseudocumene**	" " 135°;	" "	0.7812 (12°)
Hexahydrocymene, see Terpenes, p. 307, and B. **29**, 317.			

Hexahydrobenzene (B. **28**, 1234), hexahydrotoluene, hexahydro-m-xylene, and hexahydropseudocumene have been found in the naphtha of Caucasian petroleum, while hexahydrotoluene, hexahydro-m-xylene, hexahydrocumene, and hexahydrocymene are present in resin-oil.

Hexahydrobenzene, *Naphthene*, *Hexamethylene*, *Ring-hexene*, *Cyclohexane*, $CH_2<\begin{smallmatrix}CH_2.CH_2\\CH_2.CH_2\end{smallmatrix}>CH_2$, results from the reduction of iodhexamethylene (p. 291, and B. **28**, 1022; **30**, 391), and by the action of sodium upon synthetic hexamethylene bromide. It is a liquid with an odor like that of petroleum (A. **278**, 110; B. **27**, 216).

Hexahydrotoluene, *Heptanaphthene*, *Methylcyclohexane*, has also been made from suberyl alcohol (p. 28) by the action of HI at 140° (B. **25**, R. 858), and from perseïte (see 1), as well as from synthetic methyl hexamethylene ketone by means of the corresponding alcohol (B. **29**, 731). Bromine and aluminium bromide convert it into **pentabromtoluene**, melting at 282°.

Hexahydro-m-xylene, *Octonaphthene*, [1,3-*Dimethylcyclohexane*], is obtained from camphoric acid, from heptanaphthene carboxylic acid by means of HI (A. **225**, 110; B. **24**, 2718; **25**, 920), and from hexahydro-2,6-dimethyl phenol (p. 294).

Hexahydro-p-xylene is obtained from brom-camphor by means of $ZnCl_2$ at 160° (B. **13**, 1407).

Hexahydropseudocumene, *Nonaphthene*, 1,3,4-*Trimethylhexamethylene*, from hexahydrotrimethyl phenol (B. **29**, 215), when acted upon with bromine and aluminium bromide, yields tribrompseudocumene. 1,3-**Methylisopropylcyclohexane**, sym. *menthane*, boiling at 167°, is formed by the reduction of its iodine substitution product.

[1,3]-**Diethylhexahydrobenzene**, boiling at 170°, sp. gr. 0.7957 (22°/4°), n_D = 1.4388 (20°), is isomeric with hexahydrocymene. It is obtained from hexahydro-2,6-diethyl phenol (p. 294).

Halogen Substitution Products of the Hexahydrobenzenes.—*Formation:* (1) From the hexahydrobenzenes by the introduction of chlorine. (2) By the addition of halogens and halogen hydrides to di- and tetrahydrobenzenes. (3) By the addition of halogens to benzenes and halogen benzenes (p. 57). (4) From the oxyhexahydrobenzenes through the exchange of hydroxyl groups for halogens.

The third method has brought to light peculiar isomeric phenomena. *Two* isomeric benzene hexachlorides, *two* isomeric chlorbenzene hexachlorides and benzene hexabromides have been found. The disposition on the part of chemists is to ascribe the cause of this isomerism to the different positions of the attached chlorine atoms with

reference to the plane of the carbon ring, as in the case of the isomeric trithioaldehydes (1, 203), and the isomeric tri-, tetra-, and pentamethylene dicarboxylic acids (pp. 23, 24, 27). At the conclusion of the hexahydrobenzenes only those addition products obtained according to method 3 will be discussed, which eventually, by loss of halogen hydride, pass into benzene halogen substitution products.

α- or **trans-Benzene Hexachloride**, $C_6H_6Cl_6$, melting at 157° and boiling at 218° (345 mm.), decomposes into 3HCl and unsym. trichlorbenzene (p. 58). β- or **cis-Benzene Hexachloride** melts and sublimes near 310°. α-Benzene hexachloride was made by the action of chlorine upon benzene in sunlight (1825, Faraday; 1835, Mitscherlich, Pogg. A. **35**, 370). α- and *β-Benzene hexachlorides* are produced when chlorine is conducted into boiling benzene (1884, Meunier; B. **18**, R. 149; **19**, R. 348), or, better, into a mixture of benzene and 1 per cent. sodium hydroxide. The α-body is separated by distillation in steam from the less volatile β-derivative (B. **24**, R. 632), or by means of chloroform from the more sparingly soluble β-compound. The latter is the more resistant of the two modifications. When heated with alcoholic potash it is converted with greater difficulty than the α-body into unsym. trichlorbenzene. It is not affected by alcoholic potassium cyanide, but when boiled with this reagent the α-variety is converted into unsym. trichlorbenzene. Zinc in alcoholic solution changes the α-modification into benzene (Z. f. Ch., 1871, N. F. 7, 284, 293).

α- and **β-Chlorbenzene Hexachloride**, $C_6H_5Cl_7$, melting at 146° and 260°, yield 1,2,3,5-tetrachlorbenzene with alcoholic potash (A. **141**, 101; B. **25**, 373). **1,2,4-Trichlorbenzene Hexachloride**, $C_6H_3Cl_9$, melts at 95°.

α-**Benzene Hexabromide**, $C_6H_6Br_6$, melting at 212°, results from the action of bromine upon benzene in sunlight, and when bromine acts upon boiling benzene. When it splits off HBr, 1,2,4-tribrombenzene is formed (Pogg. A. **35**, 374). It is isomorphic with α-benzene hexachloride (B. **18**, R. 553). When bromine acts upon benzene in the presence of dilute caustic soda, a second compound—*β-Benzene Hexabromide*, melting at 253° (B. **29**, R. 1138)—is formed together with the first body.

1 b. TETRAHYDROBENZENES, NAPHTHYLENES [CYCLOHEXENES].

Tetrahydrotoluene has been discussed together with hexahydrotoluenes and allied hydrocarbons found in the essence of resin. The hexahydrobenzenes yield tetrahydrobenzenes by the introduction of chlorine and the exit of HCl. The hydrocarbons—*e. g.*, *Carvomenthene* and *Menthene* (see these)—obtained from terpenes and their derivatives belong to the tetrahydrobenzenes.

Tetrahydrobenzene, $CH_2<\begin{matrix}CH_2—CH\\CH_2—CH_2\end{matrix}>CH$, boiling at 82–84° (p. 291), is produced on distilling monobromhexamethylene (p. 294) with quinoline. It is a colorless liquid, resembling petroleum. It has less of the leek odor than dihydrobenzene. It is colored yellow by concentrated sulphuric acid. The *dibromide* is a liquid. The *nitrosochloride* melts at 152°. The *nitrosate*, $NO.C_6H_{10}.O.NO_2$, melts at 150° with decomposition (A. **278**, 107). *Tetrahydrotoluene* is obtained from pulegone (A. **289**, 343).

Different homologous tetrahydrobenzenes have been obtained from hexahydrophenols (p. 294) by the removal of water with P_2O_5. **Methyl-, dimethyl-, Methyl-isopropyl-tetrahydrobenzenes** boil at 105°, 124°, and 109° (communicated by E. Knövenagel).

1 c. DIHYDROBENZENES [CYCLOHEXADIËNES].

Very probably some of the naturally occurring terpenes belong to the dihydrobenzenes. The artificially prepared representatives of the dihydrobenzenes are very similar in deportment to them. The method of preparing the simplest of the hydrocarbons in this class—dihydrobenzene—from succino-succinic ester has already been discussed (p. 291). Mono-alkyl and di-p-alkyl-dihydrobenzenes were made in like manner from mono- and di-alkylsuccinosuccinic esters (B. **26**, 232).

A second method for the preparation of dihydrobenzenes is based upon the rearrangement of the dihydroresorcinol derivatives obtained in the condensation of δ-ketonic esters (p. 297). The dihydroresorcinols yield dihydric alcohols upon reduction ; these, by the exit of two molecules of water, become dihydrobenzenes. Thus far only one phenyldihydrobenzene has been prepared in this manner (A. **289**, 137).

Dihydrobenzene, [Cyclohexadiën], $CH{\diagup CH\,.\,CH_2 \diagdown \atop \diagdown CH_2\,.\,CH \diagup}CH$ or $CH{\diagup CH_2\,.\,CH_2 \diagdown \atop \diagdown CH\,.\,CH \diagup}CH$, boiling at 84–86°, results when p dibromhexamethylene is heated with quinoline (p. 291). It is a leek-like liquid, resembling benzene. It resinifies, like the terpenes (p. 291), on exposure to the air. It decolorizes a solution of $KMnO_4$ instantaneously, and takes on a blue color when treated with concentrated sulphuric acid (see sylvestrene, p. 308). Its *tetrabromide* melts at 185° (B. **25**, 1840).

Dihydrotoluene, C_7H_{10}, boiling at 105–108°, is obtained from toluene by the action of PH_4I (A. **155**, 271).

Dihydro-o-xylene, *Cantharene*, boiling at 135°, is produced when cantharic acid, $C_{10}H_{12}O_4$, a rearrangement product of cantharadine, is distilled with caustic lime. Its odor is like that of a terpene, and it resinifies on exposure to the air (Piccard, 1878; B. **25**, 2453).

Dihydro-m-xylene, boiling at 133°, sp. gr. 0.8275 (20°), is obtained when methyl heptenone, $(CH_3)_2CH\,.\,CH = CH\,.\,CH_2COCH_3$, is condensed with $ZnCl_2$ (A. **258**, 326).

Dihydro-p-xylene boils at 134°. **Dihydro-p-diethyl Benzene** boils at 180–185°. **Dihydro-p-methylisopropyl Benzene**, *Dihydro*-p-*cymene*, boils at 174°.

2. RING-ALCOHOLS OF THE HYDROAROMATIC HYDROCARBONS.

In this group are included quercite and inosite, formerly classed with the sugars, as well as the ring alcohols of the terpane or menthane group among the terpenes (p. 313), while other members have been obtained by the reduction of aromatic or hydroaromatic compounds, but chiefly from the corresponding ketones.

Hexahydrophenol, [Cyclohexanol], $C_6H_{11}(OH)$, melting at +15° and boiling at 158° (720 mm.), is formed by the action of zinc-dust and glacial acetic acid upon p-iodhexahydrophenol, the reaction product obtained from quinite and hydriodic acid. Its odor is like that of fusel oil. It is more readily soluble in water than the aliphatic alcohols containing six C-atoms (B. **26**, 229). Its *acetyl derivative* melts at 104°. Hydrobromic acid converts it into *bromcyclohexane*, boiling at 162° (720 mm.). See tetrahydrobenzene.

Hexahydro-2,6-dimethyl Phenol, boiling at 174°, and **Hexahydro-2,6-diethyl Phenol**, melting at 77° and boiling at 210°, along with a series of additional homologues, have been prepared by the reduction of the corresponding ketones (p. 296).

Hexahydrophenols have also been obtained from the synthetic keto-R-hexenes (p. 298). This has been accomplished by treating the latter with sodium and alcohol. The hexahydrophenols appear to occur in two probably stereoisomeric forms. A chromic acid mixture oxidizes them to *keto*-R-*hexanes*. Their hydriodic esters are reduced by zinc-dust and glacial acetic ester to *cyclohexanes*, and when they lose water through the action of P_2O_5, *cyclohexenes* result (privately communicated by E. Knövenagel).

Quinite, [Cyclohexane-1,4-diol], $HOCH{<}{CH_2 - CH_2 \atop CH_2 - CH_2}{>}CHOH$, melting at 144°, is formed from p-diketohexamethylene (p. 296) when treated with sodium amalgam in the presence of carbon dioxide. This was demonstrated by A. v. Baeyer in 1892. It tastes sweet at first, then bitter, and is readily soluble in water and in alcohol. Chromic

acid oxidizes it to quinone (B. **25**, 1038). Quinite serves for the preparation of the simple hydride derivatives of benzene (B. **26**, 229). Hydriodic acid converts it into **p-iodcyclohexanol** and **p-di-iodcyclohexane**. By reduction the first yields hexahydrophenol, the second cyclohexane (p. 293). **p-Dibromcyclohexane** passes readily into *dihydrobenzene* (p. 294) (B. **26**, 230). **2,5-Dimethyl Quinite** is formed from the corresponding diketone (B. **25**, 2122).

Phloroglucite, s-*Trioxyhexamethylene*, [*Cyclohexane-1,3,5-triol*], $HOCH{<}\begin{matrix}CH_2-CH(OH)\\CH_2-CH(OH)\end{matrix}{>}CH_2 + 2H_2O$, melts when anhydrous at 184°. It is formed when phloroglucin is reduced in an approximately neutral solution with sodium amalgam (B. **27**, 357).

Quercite, [*Cyclohexanpentol*], $CH_2{<}\begin{matrix}CH(OH)-CH(OH)\\CH(OH)-CH(OH)\end{matrix}{>}CH(OH)$, melting at 235°, $[\alpha]_D = +24.16°$, occurs in acorns. The aqueous extract of the latter can be freed of glucoses by fermentation with beer-yeast. Quercite does not ferment with yeast. Hydriodic acid converts it into benzene, hexane, phenol, quinone, and hydroquinone (Prunier). Nitric acid oxidizes it to mucic acid and trioxyglutaric acid (see vol. 1). A solution of potassium permanganate converts it chiefly into malonic acid, although oxalic acid and carbonic acid are formed simultaneously (B. **29**, 1762).

Inosite, *Hexahydrohexaoxybenzene*, [*Cyclohexanhexene*], $C_6H_6(OH)_6$, is known in one optically inactive and two optically active modifications.

i-Inosite, *Phaseomannite*, *Dambose*, $C_6H_6(OH)_6 + 2H_2O$, melts at 225° when anhydrous. It occurs in the muscles of the heart and in the urine when there has been an excessive consumption of water; also in unripe beans (*Phaseolus vulgaris*) and peas. If heated to 170° with hydriodic acid, it yields phenol, di-iodphenol, and traces of benzene (Maquenne). Concentrated nitric acid oxidizes it to di- and tetra-oxyquinones (p. 170), and to rhodizonic acid (p. 171) (B. **20**, R. 478; **23**, R. 26).

Dambonite, $C_6H_6(OH)_4(OCH_3)_2 + 3H_2O$, is the dimethyl ether of i-inosite. It occurs in the caoutchouc from Gabon. **i-Inosite Hexaacetate** melts at 211°.

d-Inosite, melting at 247°, $[\alpha]_D = +65°$, from pinite by the action of hydriodic acid, behaves like i-inosite with nitric acid. **Pinite,** *Matezite*, $C_6H_6(OH)_5(OCH_3)$, melting at 186°, $[\alpha]_D = +65.51°$, is present in the juice of *Pinus lambertina*, also in the caoutchouc from *Mateza roritina* of Madagascar.

l-Inosite, melting at 238°, $[\alpha]_D = -55°$, from quebrachite by means of hydriodic acid, behaves toward nitric acid just like i-inosite. **Quebrachite,** $C_6H_6(OH)_5OCH_3$, melting at 186°, $[\alpha]_D = -80°$, occurs in the quebracho-bark.

Phenose, $C_6H_6(OH_6)$ (?), is an amorphous, readily soluble substance, deliquescing in the air. It has a sweet taste and reduces Fehling's solution, but is not capable of fermentation. It has been obtained by the action of a soda solution (A. **136**, 323) upon the addition product of benzene with three molecules of hypochlorous acid, $C_6H_6\begin{cases}Cl_3\\(OH)_3\end{cases}$.

Ring-alcohols of Tetrahydrobenzene: **Tetrahydrophenol,** [Δ_3-Cyclohexenol],*

$CH{\Large\diagup\!\!\diagup}\begin{matrix}CH-CH_2\\ \\CH_2-CH_2\end{matrix}{>}CHOH$, boiling at 163°, is formed when p-iodcyclohexanol (p. 291) is distilled with quinoline.

3. RING-AMINES OF THE HYDROAROMATIC HYDROCARBONS

have been obtained by the reduction of the corresponding oximes with sodium in alcoholic solution. The ring-amines of the terpane and menthane groups, discussed under the terpenes, belong in this class. **Amidohexamethylene,** $C_6H_{11}NH_2$, is isomeric with the methyl piperidines. It boils at 133°, smells like coniïne, and dissolves sparingly in

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* Δ indicates a double union; the added number (in this case β) that this carbon atom 3 is doubly linked to the carbon atom 4.

water. Its *acet-derivative* melts at 104°. The *benzoyl compound* melts at 147°. The *phenylurea derivative* melts at 180°. The *phenylthiourea* body melts at 147°.

o-Diamidohexamethylene, $C_6H_{10}[1,2](NH_2)_2$, is an oil, boiling at 183–185°. It results when the amide of hexahydroanthranilic acid (p. 300) is treated with sodium hypobromite and then with hydrochloric acid. Like the aromatic o-diamines, it unites with benzaldehydes, forming aldehydines (p. 95) (A. **295**, 187).

m-Diamidohexamethylene, boiling at 193°, smells like ethylenediamine. It is soluble in water. Nitrous acid decomposes it into nitrogen and dihydrobenzene (A. **228**, 39). The *diacet-compound* melts at 256°.

p-Diamidohexamethylene, $C_6H_{10}[1,4](NH_2)_2$, is a liquid (B. **27**, 1449).

4. RING-KETONES OF THE HYDROAROMATIC HYDROCARBONS.

(*a*) **Ring-ketones of Hexahydrobenzenes.—Pimelin Ketone,** [Cyclohexanon], *Ketohexamethylene*, $CH_2 < \begin{matrix} CH_2-CH_2 \\ CH_2-CH_2 \end{matrix} > CO$, boiling at 155°, is an oil with an odor like peppermint. It results (1) by the oxidation of hexahydrophenol (p. 294); (2) in the reduction of phenol with alternating currents; (3) in the distillation of calcium n-pimelinate (1, 455). Upon reduction it yields [cyclohexanol] (p. 294), while nitric acid oxidizes it to *adipic acid* (1, 455). Its *oxime* melts at 88°. Its *phenylhydrazone*, melting at 74–77°, when acted upon by mineral acids loses ammonia and passes into tetrahydrocarbazole (see this) (A. **278**, 100).

A series of alkylic keto-hexamethylenes has been obtained from the alkylic pimelic acids:

2-, 3-, 4-**Methylketohexamethylenes** boil at 166°, 164°, and 163–165°; 2,6-**Dimethyl-** and 2,6-**Diethylketohexamethylenes** boil at 163° and 206°; 2,4,5-**Trimethylketohexamethylene** boils at 191° (B. **28**, 1341, 2944; **29**, 731; A. **295**, 186). 3-Methylketohexamethylene has also been prepared in other ways. It results from the oxidation of 3-methylketohexahydrophenol with a chromic acid mixture; the latter body is produced in the reduction of synthetic 3-methylcycloketohexene (p. 298). It also appears in an optically active, dextro-gyrating modification by the decomposition of pulegon (see this), and, finally, in the decomposition of isopulegon (see this) (B. **30**, 23). A 3,5,5-**Trimethylketohexamethylene,** boiling at 189°, is *Dihydroacetophorone*. It is formed when chromic acid oxidizes dihydroisoacetophorol, a reduction product derived from isoacetophorone.

Similarly, 3,5-**Methylisopropylketohexamethylene,** sym. *Menthone*, boiling at 222°, is obtained by the oxidation of the corresponding alcohol.

Diketohexamethylenes, Cyclohexandiones.

Theory predicts three isomeric diketohexamethylenes, two of which—dihydroresorcinol and tetrahydroquinone—are known. Dihydroresorcinol possesses the character of a feeble base, and is therefore to be viewed probably as a ring-shaped, unsaturated ketone-alcohol.

Dihydroresorcinol, 1,3-*Cyclohexandion*, m-*Diketohexamethylene*, $CH_2 < \begin{matrix} CH_2.CO \\ CH_2.CO \end{matrix} > CH_2$ or $CH_2 < \begin{matrix} CH_2.CO\text{——} \\ CH_2.C(OH) \end{matrix} \gtrdot CH$, melts with decomposition at 104–106°. It is produced upon introducing pure sodium amalgam into a boiling aqueous resorcinol solution while carbon dioxide is being conducted into it. It may be synthesized by the condensation of γ-acetylbutyric ester with sodium ethylate (p. 44). Dihydroresorcinol dissolves readily in water, alcohol, and chloroform, but with difficulty in ether. When heated to 150–160° with baryta-water it is decomposed so as to form γ-acetylbutyric acid, and when oxidized it yields glutaric acid and carbon dioxide (A. **294**, 269). It reacts acid and decomposes the alkali and alkaline earth carbonates. It also forms a *dioxime*, $C_6H_8(NOH)_2 + 2H_2O$. This melts at 154–157° when it is anhydrous; when

reduced it becomes m-diamidohexamethylene. m-Dioxyhexahydroisophthalo nitrile (p. 304) (A. **278**, 20) is formed by adding prussic acid to dihydroresorcinol.

Homologues of dihydroresorcinol are similarly formed in the condensation of like δ-ketone-carboxylic esters, as, for example, in the addition of malonic esters to alkylidene-acetoacetic ester. When the latter is condensed with malonic ester through the agency of sodium ethylate, and the product then saponified, carbon dioxide is eliminated and there results **methyldihydroresorcinol**, melting at 126° (A. **289**, 137; **294**, 253):

$$\begin{array}{l}\quad\;\; CH_3 \\ CO_2RCH\,.\,\overset{|}{C}H\,.\,CH\,.\,CO_2R \\ \quad \overset{|}{C}O\,.\,CH_3\,\overset{|}{C}O_2R\end{array} \longrightarrow \begin{array}{l}\qquad\qquad\; CH_3 \\ CO_2R\,.\,CH\,.\,\overset{|}{C}H\,.\,CH\,.\,CO_2R \\ \qquad \overset{|}{C}O\,.\,CH_2\,.\overset{|}{C}O\end{array} \longrightarrow \begin{array}{l}\qquad\; CH_3 \\ CH_2\,.\,\overset{|}{C}H\,.\,CH_3 \\ \overset{|}{C}O\,.\,CH_2\,.\,\overset{|}{C}O.\end{array}$$

Phenyldihydroresorcinol melts at 184° with decomposition. **Dimethyldihydroresorcinol**, $(CH_3)_2C:[CH_2.CO]_2:CH_2$, melts at 150°.

The homologous dihydroresorcinols react like simple dihydroresorcinol, both as diketones and as unsaturated oxyketones.

Tetrahydroquinone, [1,4-*Cyclohexandion*], p-*Diketohexamethylene*, $CO{<}{\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}}{>}CO$, melting at 78°, results upon saponifying succino-succinic ester with concentrated sulphuric acid, when it loses carbon dioxide (Baeyer, see p. 291), or when the same body is boiled with aqueous-alcoholic hydrochloric acid (private communication from R. Stollé). It unites with sodium bisulphite to a *dioxime*, melting at 192°; compare p-diamidohexamethylene. It forms *quinite* (p. 294) upon reduction; see also α-dioxyhexahydroterephthalic acid (p. 304).

p-Dimethyl-p-diketohexamethylene, [2,5 *Dimethyl*-1,4-*cyclohexandion*], melting at 93°, is obtained from p-dimethylsuccino-succinic ester (B. **25**, 2122).

[*Cyclohexantriones.*] Phloroglucin yields derivatives which can be deduced from the formula of 1,3,5-trioxybenzene, and others which can be obtained from the formula of 1,3,5-triketohexamethylene. It was discussed at the conclusion of pyrogallol and oxyhydroquinone (pp. 164, 165), as were the hexa-alkyl derivatives of phloroglucin.

Triquinoyl, $C_6O_6 + 8H_2O$ (p. 171), described with the quinones, is probably **hexaketohexamethylene.**

Halogen Substitution Products of the Ring-ketones of Hexahydrobenzene.—These are formed in the continuous action of chlorine and bromine upon phenols, quinones and oxyquinones. Several of the keto-chlorides can be readily rearranged into halogen keto-pentene derivatives, and be decomposed into highly chlorinated fatty bodies: ketones, ketonic acids, and fatty acids (pp. 44–47).

Heptachlor-resorcinol, [*Heptachlor*-1,3-*cyclohexandion*], $CHCl{<}{\begin{matrix}CCl_2-CO\\CCl_2-CO\end{matrix}}{>}CCl_2$, melting at 50° and boiling at 170° (25 mm.), is produced in the action of chlorine upon resorcinol in chloroform (B. **24**, 912). Decomposition, p. 45.

Quinone Tetrabromide, [2,3,5,6-*Tetrabromcyclohexandion*], $CO{<}{\begin{matrix}CHBr.CHBr\\CHBr.CHBr\end{matrix}}{>}CO$ (p. 168). **Hexachlortriketo-R-hexylene**, [*Hexachlor*-1,3,5-*cyclohexantrion*], $CCl_2{<}{\begin{matrix}CO-CCl_2\\CO-CCl_2\end{matrix}}{>}CO$, melting at 48° and boiling at 268° (760 mm.), 150° (19 mm.), results from the action of chlorine upon phloroglucin in chloroform solution (B. **22**, 1473). Decomposition—see p. 44.

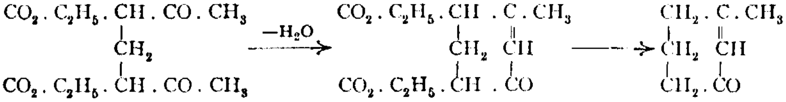
Pentabromdiketo-oxy-R-hexene Hydrate, $CBr_2{<}{\begin{matrix}CO-CBr_2\\CO-CBr\end{matrix}}{>}C.OH + H_2O$, melts at 119° with decomposition. It is produced when bromine in water acts upon phloroglucin. It forms amber-yellow-colored crystals. It is a strong acid.

Hexabromtriketo-R-hexylene, $C_6Br_6O_3$, melts at 147° (B. **23**, 1729).

Tri- and Tetrachlortetraketohexamethylene, $CCl_2{<}{\begin{matrix}CO-CO\\CO-CO\end{matrix}}{>}CCl_2$, melt at 150° with decomposition, and at 60°. They are obtained from chloranilic acid and

chlorine. *The corresponding bromine derivatives are made from bromanilic acid* (B. **25**, 845).

b. Ring-ketones from the Tetrahydrobenzenes can be synthesized by condensing acetoacetic ester, acetone dicarboxylic ester, and analogous compounds with aldehyde iodides, like methylene iodide, or with aldehydes in the presence of small quantities of bases, such as diethylamine or piperidine, to 1,5-diketone-carboxylic esters—*e. g.*, methylene-, ethidene-, isobutylidenediacetoacetic ester and methylenebisacetonedicarboxylic ester. When the latter are treated with hydrochloric acid in ether, they first form a ring and become carboxylic esters of Δ_2-keto-R-hexenes, and then, when acted upon with alkalies or dilute acids, are saponified, split off CO_2, and change to the ketones themselves (A. **289**, 131):



3-Methyl-Δ_2-keto-R-hexene, boiling at 200°, is a mobile liquid with an agreeable odor. Its bromine addition product decomposes spontaneously into HBr and m-cresol. Its *oxime* melts at 63° and boils at 130° (18 mm.) (A. **288**, 355).

3,5-Dimethyl-Δ_2-keto-R-hexene boils at 211°. Its dibromide changes quite readily into sym. xylenol (p. 144) (A. **281**, 121).

3,5,5-Trimethyl-Δ_2-keto-R-hexene, Isoacetophorone, *Isophorone*, $(CH_3)_2C\langle{}^{CH_2.CO}_{CH_2.C=\!=\!CH_3}\rangle CH$, boiling at 89° (10 mm.), is produced in the condensation of mesityl oxide with acetoacetic ester, saponification, and elimination of carbon dioxide from the carboxylic ester formed at first. It also results from the condensation of acetone by means of lime or sodium ethylate. It is isomeric with phorone (1, 221), camphorphorone (see this), and isocamphorone (see this). Upon reduction with sodium and alcohol it forms *dihydroisophorol*, $C_9H_{17}(OH)$, which by loss of water becomes *trimethylcyclohexene*, and by the reduction of its iodide yields *trimethylcyclohexane*. When oxidized with potassium permanganate the ring is ruptured and various acids result: $C_9H_{14}O_4$, $C_8H_{14}O_3$, and finally $C_6H_{10}O_4$, unsym. dimethylsuccinic acid (private communication from J. Bredt and Rübel, and E. Knövenagel; compare A. **290**, 123).

3-Methyl-5-isopropyl-Δ_2-keto-R-hexene, $C_3H_7.CH\langle{}^{CH_2.CO}_{CH_2.C(CH_3)}\rangle CH$, boils at 244°. Its dibromide passes readily into sym. carvacrol (p. 145) (B. **26**, 1089; **27**, 2347; A. **288**, 357).

3-Methyl-5-isobutyl- and **3-methyl-5-hexyl-Δ_2-keto-R-hexene** boil at 147° and at 167° (22 mm.) (B. **288**, 336, 344).

Those chemists who consider the quinones to be ketones regard *rhodizonic acid* (p. 171) as a tetraketotetrahydrobenzene derivative.

Halogen substitution products of ring-ketones of tetrahydrobenzenes result when chlorine acts upon phenols, anilines, oxybenzoic acids, etc. They can be very readily torn asunder (pp. 44–47).

Heptachlorketotetrahydrobenzenes, $CCl_2\langle{}^{CCl = CCl}_{CHCl.CCl_2}\rangle CO$ and $CCl\langle{}^{CCl - CCl_2}_{CHCl - CCl_2}\rangle CO$, the α-body melting at 98° and the β-modification at 80°, result from the action of chlorine upon m-chloraniline (B. **27**, 547).

Octochlorketotetrahydrobenzene, $CCl_2\langle{}^{CCl = CCl}_{CCl_2 - CCl_2}\rangle CO$, or $CCl\langle{}^{CCl - CCl_2}_{CCl_2 - CCl_2}\rangle CO$, melting at 103°, result from the action of chlorine upon pentachlorphenol in glacial acetic acid, and from perchlor-m-oxybenzoic acid. Reducing agents change it into pentachlorphenol (B. **27**, 550).

Hexachlor-o-diketo-R-hexene, $CCl_2<\begin{matrix}CCl_2 - CO\\ CCl = CCl\end{matrix}>CO + 2H_2O$, melts at 93° with decomposition. It is formed when chlorine acts upon pyrocatechol and o-amidophenol chlorhydrate dissolved in acetic acid. Stannous chloride reduces it to cyclobenzoquinone (p. 167). See p. 44 for its decomposition and conversion into a cyclopentene derivative. Homologous o-diketochlorides have been obtained from o-diamidomethyl benzenes (B. **27**, 560).

Pentachlor-m-diketo-R-hexene, $CCl<\begin{matrix}CO - CCl_2\\ CH - CCl_2\end{matrix}>CO$, melting at 92° and boiling at 160° (25 mm.), results when chlorine acts upon resorcinol in chloroform (B. **23**, 3777). See p. 45 for its decomposition.

Hexachlor-m-diketo-R-hexene, $CCl_2<\begin{matrix}CO - CCl_2\\ CH = CCl\end{matrix}>CO$, melting at 115° and boiling at 159° (14 mm.), is produced when chlorine acts upon 3,5-dioxybenzoic acid dissolved in glacial acetic acid (B. **25**, 2688).

Hexachlor-p-diketo-R-hexene, $CO<\begin{matrix}CCl_2 - CCl_2\\ CCl = CCl\end{matrix}>CO$, melting at 89° and boiling at 184° (45 mm.), is formed when chlorine acts upon p-amidophenol hydrochloride in glacial acetic acid (A. **267**, 16). See p. 45 for its decomposition.

c. **Ring-ketones of the Dihydrobenzenes.**—There are two possible dihydrobenzenes, and from each one mono-ketone can be obtained. Both bodies are not yet known, but in *tetrachlorketodihydrobenzene*, $CCl<\begin{matrix}CH - CCl_2\\ CH = CCl\end{matrix}>CO$, or $CCl_2<\begin{matrix}CH = CCl\\ CH = CCl\end{matrix}>CO$, melting at 122°, and in *hexachlorketodihydrobenzene*, $CCl<\begin{matrix}CCl = CCl\\ CCl - CCl_2\end{matrix}>CO$, melting at 106°, we have chlorine derivatives of one or of both ketodihydrobenzenes. The first body is formed from trichlorphenol and chlorine, and the second, most conveniently, by heating (B. **27**, 546) the heptachlorketotetrahydrobenzene, melting at 98°, and by treating phenol, anisol, and pentachloraniline with chlorine (B. **28**, R. 63).

Carvone, described after the terpenes, is very probably a ketodihydro-p-cymene.

Each of the possible dihydrobenzenes also yields a diketone:

$CH<\begin{matrix}CH - CH_2\\ CH = CH\end{matrix}>CH_2$ o-Dihydrobenzene $\quad CH_2<\begin{matrix}CH = CH\\ CH = CH\end{matrix}>CH_2$ p-Dihydrobenzene

$CH<\begin{matrix}CH - CO\\ CH = CH\end{matrix}>CO$ o-Benzoquinone, o-Diketodihydrobenzene. $\quad CO<\begin{matrix}CH = CH\\ CH = CH\end{matrix}>CO$ p-Benzoquinone, p-Diketodihydrobenzene.

If the diketone formula is preferred for the benzoquinones, previously discussed with the phenols (pp. 166–175), then p-benzoquinone is p-diketodihydrobenzene, and its numerous derivatives are also deducible from the latter compound. o-Benzoquinone would be o-diketodihydrobenzene. It is only known in its tetrahaloid substitution products, which were discussed under the benzoquinones before the para-quinones.

5. HYDROAROMATIC CARBOXYLIC ACIDS.

Attached to the hydroaromatic hydrocarbons, ring-alcohols, ring-amines, and ring-ketones are numerous hydroaromatic carboxylic acids, their corresponding hydroaromatic alcohols, aldehydes, and ketones, which, however, have only been prepared in very special cases. In addition to the simple carboxylic acids, oxy- and keto-carboxylic acids are also known. *Shikimic* and *quinic acids* belong to the first class (p. 301), while in the second class we find succino-succinic ester (p. 305) and

other important ketone-carboxylic esters, which are of great value in the synthesis of the simple hydroaromatic derivatives (p. 302).

1. HYDROAROMATIC MONOCARBOXYLIC ACIDS.

A (1). **Hexahydrobenzoic Acids, Hexamethylene Carboxylic Acids,** *Naphthenic Acids*, have been obtained by the reduction of boiling amyl or capryl alcohol solutions of benzoic acid and its homologues with metallic sodium, or by reducing the solution of sodium benzoate with sodium in an atmosphere of CO_2 (B. **24**, 1865; **25**, 3355). So far as present experience warrants they are isomeric and not identical (B. **27**, R. 195, 197) with the "natural naphthenic acids" occurring in the oil which issues from the earth in and about Baku. Just as fatty acids have been prepared from malonic acids, so hexamethylene monocarboxylic acids have been obtained by heating hexamethylene-1,1-dicarboxylic acids (p. 302). The latter bodies have been prepared synthetically.

The hexamethylenecarboxylic acids are weak acids. They are reduced, when heated with hydriodic acid, to hexahydroaromatic hydrocarbons—*naphthenes*, containing a like number of C-atoms in the molecule. Hence they are also designated as *naphthenic acids*.

Hexahydrobenzoic Acid, *Naphthenic Acid*, $C_6H_{11}.CO_2H$, melting at 28° and boiling at 232°, results from the reduction of benzoic acid (see this), Δ_2-tetrahydrobenzoic acid (A. **271**, 261), p-dimethylamidobenzoic acid (B. **27**, 2829), and cyclohexanol-1-carboxylic acid (B. **27**, 1231); also by heating hexamethylene-1,1-dicarboxylic acid. The *calcium salt*, $(C_7H_{11}O_2)_2Ca + 5H_2O$. The *methyl ester* boils at 182°. The *ethyl ester* boils at 194°, and the *amide* melts at 185°.

Hexahydro-o-*toluic Acid* melts at 51° and boils at 241°.
Hexahydro-m-*toluic Acid* is a liquid, boiling at 245°.
α-Hexahydro-p-*toluic Acid* melts at 110° and boils at 246°.
β-Hexahydro-p-*toluic Acid* is a liquid.

These four acids have been obtained by the reduction of the three toluic acids (J. pr. Ch. [2], **49**, 65; B. **27**, R. 195). The last acid was also obtained by reducing Δ_3-dibromtetrahydrotoluic acid, the addition product of 2HBr to p-methylenedihydrobenzoic acid (see this) (A. **280**, 156), and hexahydro-o-toluic acid also from 2-methylhexamethylene-1,1-dicarboxylic acid (p. 302), and from 2 methyl-1-acetylhexamethylene-carboxylic ester (p. 302).

α-Monobromhexahydrobenzoic Acid, melting at 63°, and **α-Monobromhexahydro-p-toluic Acid,** melting at 71°, are produced by acting with bromine upon the chlorides of the corresponding hexahydro-acids.

Hexahydroanthranilic Acid, o-*Amidohexahydrobenzoic Acid*, $NH_2[2]C_6H_{10}.CO_2H$, melts with decomposition at 274°. It is formed along with pimelic and hexahydrobenzoic acids in the reduction of anthranilic acid (B. **27**, 2470; A. **295**, 187). **Hexahydro-p-dimethylamidobenzoic Acid** (B. **27**, 2831).

Derivatives of o-amidohexahydrophenylacetic acid and propionic acid result in oxidizing dekahydroquinoline compounds with potassium permanganate.

Octohydrocarbostyril, $C_6H_{10}\left\{\begin{matrix}CH_2.CH_2\\ NH.CO\end{matrix}\right.$ (with CH_2 bonded to CO), melting at 151°, is poisonous (B. **27**, 1472).

A (2). **Tetrahydrobenzoic Acids can be obtained from the α-monobromhexahydro-acids** (see above) by splitting off HBr with alkalies, or by means of quinoline (A. **271**, 207; **280**, 163), and also by the reduction of the benzoic acids and dihydrobenzoic acids (B. **26**, 457).

Δ_1-Tetrahydrobenzoic Acid, $CH_2\begin{matrix}\diagup CH_2.CH_2 \diagdown\\ \diagdown CH_2.CH_2 \diagup\end{matrix}C.CO_2H$, is formed from α-bromhexahydrobenzoic acid and from Δ4,6-dihydrobenzoic acid.

Δ_3-Tetrahydrobenzoic Acid, *Benzoleïnic Acid*, $CH_2<\begin{matrix}CH=CH\\ CH_2-CH_2\end{matrix}>CH.CO_2H$, is a liquid boiling at 234° (A. **271**, 234; B. **27**, 2471). It is formed from benzoic acid.

Δ_1-Tetrahydro-p-toluic Acid melts at 132°.

Isogeranic Acid, $CH\begin{matrix}\nearrow CH - CH(CH_3)\searrow \\ \searrow CH_2 - C(CH_3)_2\nearrow\end{matrix}CH.CO_2H$ (?), melting at 103° and boiling at 138° (*11 mm.*), results when geranic acid (I, 289; II, 310) is acted upon with concentrated sulphuric acid (B. 27, R. 768).

A (3). **Dihydrobenzoic Acids.—Δ4,6-Dihydrobenzoic Acid,** $CH\begin{matrix}\nearrow CH . CH\searrow \\ \searrow CH_2 . CH_2\nearrow\end{matrix}C.CO_2H$, melting at 94°, is produced in the oxidation of *dihydrobenzaldehyde*, boiling at 121–122°, with silver oxide. The latter body is formed by decomposing anhydroecgonine-dibromide with sodium carbonate (B. 26, 454). A different dihydrobenzoic acid, melting at 73°, is obtained from Δ_2-tetrahydrobenzoic acid dibromide (B. 24, 2622). **Dihydrocumic Acid,** *p-Isopropyldihydrobenzoic Acid*, $C_6H_6(C_3H_7)COOH$, melting at 130–133°, is formed when nopic acid, an oxidation product of turpentine oil (see this), is boiled with sulphuric acid (B. 29, 1926).

B. **Hexahydro-oxybenzoic Acids.—α-Oxyhexamethylene Carboxylic Acid,** *α-Oxyhexahydrobenzoic Acid, Cyclohexanol-1-carboxylic Acid*, $CH_2\begin{matrix}\nearrow CH_2-CH_2\searrow \\ \searrow CH_2-CH_2\nearrow\end{matrix}C\begin{matrix}\nearrow CO_2H \\ \searrow OH\end{matrix}$, melting at 106°, is formed when cyclohexanon (p. 296) in ether is treated with prussic and hydrochloric acids; see also hexahydrobenzoic acid.

Hexahydrosalicylic Acid, *(β-) Hexahydro-o-oxybenzoic Acid*, $CH_2<\begin{matrix}CH_2 . CH(OH) \\ CH_2 . CH_2\text{———}\end{matrix}>CH.CO_2H$, melting at 111°, results when nitrous acid acts upon hexahydroanthranilic acid and by reducing β-ketohexamethylene-carboxylic ester (B. 27, 2472, 2476).

Hexahydro-m-oxybenzoic Acid, melting at 132°, is obtained by the reduction of m-oxybenzoic acid with sodium in ethyl alcohol (B. 29, R. 549).

Hexahydro-dioxybenzoic Acid is obtained from Δ_1-bromhexahydrobenzoic acid (A. 271, 280).

Dihydroshikimic Acid, *Hexahydrotrioxybenzoic Acid*, $(HO)_3C_6H_8.CO_2H$, melting at 175°, results when shikimic acid is reduced with sodium amalgam. Corresponding to it is **Dibromshikimic Acid,** $(HO)_3C_6H_6Br_2.CO_2H$, which upon evaporation with water changes to a *brom-lactone*, $C_7H_9BrO_5$, melting at 235°.

Quinic Acid, *Hexahydro-tetraoxybenzoic Acid*, $(HO)_4.C_6H_7.CO_2H$, melting at 162°, optically active, is present in the cinchona barks, in coffee beans, in bilberry, and in many other plants. It is obtained as a secondary product in the preparation of quinine by extracting the quinia bark. When its calcium salt has been purified by recrystallization the acid is liberated by oxalic acid. Upon distillation the acid breaks down into phenol, hydroquinone, benzoic acid, and salicylaldehyde. When boiled with water and lead peroxide it changes to hydroquinone, while manganese peroxide and sulphuric acid convert it into quinone (p. 167). Protocatechuic acid is formed when it is melted with caustic potash or soda (p. 227). Ferments decompose calcium quinate into protocatechuic acid. If the fermentation takes place with air exclusion the products are formic acid, acetic acid, and propionic acid. Quinic acid is reduced by hydriodic acid to benzoic acid. The *calcium salt* has the formula $(C_7H_{11}O_6)_2Ca + 10H_2O$. The *tetracetylethyl ester*, $C_6H_7(O.COCH_3)_4.CO_2C_2H_5$, melts at 135° (B. 22, 1462).

Inactive Quinic Acid is produced when its lactone, quinide, is boiled with milk of lime. *Calcium salt*, $(C_7H_{11}O_6)_2Ca + 4H_2O$.

Quinide, $C_7H_{10}O_5$, melting at 198°, optically inactive, results upon heating ordinary optically active quinic acid to 220–240° (B. 24, 1296).

Dioxydihydroshikimic Acid, *Hexahydro-pentaoxybenzoic Acid*, $(HO)_5C_6H_6.CO_2H$, melts at 156° with the elimination of water. It is optically inactive and is obtained from the brom-lactone, melting at 235°, which is formed in the action of baryta-water (B. 24, 1294) upon dibromshikimic acid (see above).

Shikimic Acid, *Trioxytetrahydrobenzoic Acid*, $(HO)_3C_6H_6.CO_2H$, melting at 184°, occurs in the fruit of *Illicium religiosum* (see shikimol, p. 270). Its transposition products, dihydro- and dioxydihydroshikimic acids, have been previously described.

C. **Ketohydromonocarboxylic Acids.—(o-) β-Ketohexamethylene Carboxylic**

Ester, $CH_2<\begin{matrix}CH_2 . CO\\CH_2 . CH_2\end{matrix}>CH . CO_2R$, is formed when pimelic acid ester is heated with sodium and alcohol (B. **27**, 103).

(m-) γ-**Ketohexamethylene Carboxylic Acid,** $CH_2<\begin{matrix}CO . CH_2\\CH_2 . CH_2\end{matrix}>CH . CO_2H$, is produced when tetrahydro-oxyterephthalic acid is heated to 115°, or boiled with water, or when m-oxyhexahydrobenzoic acid, in the form of its ester, is oxidized with sodium bichromate (B. **29**, R. 550).

2-**Methyl-1-acetylhexamethylene Carboxylic Ester,**
$CH_2<\begin{matrix}CH_2-CH(CH_3)\\CH_2-CH_2 \text{——}\end{matrix}>C<\begin{matrix}CO_2C_2H_5\\CO . CH_3\end{matrix}$, is obtained from methylpentamethylene dibromide and sodium acetoacetic ester. On boiling with alcoholic potash it breaks down *into 2-methylhexamethylene carboxylic acid, or hexahydro-o-toluic acid* (p. 300) and **methylhexamethylenemethyl ketone,** 2-*Methylhexahydroacetophenone*, boiling at 197–200° (B. **21**, 737).

3-**Methyl-Δ_2-keto-R-hexene-6-carboxylic Ester,**
$CH_3 . C\begin{matrix}\nearrow CH - CO \searrow\\\searrow CH_2 - CH_2 \nearrow\end{matrix}CH . CO_2C_2H_5$ $[CH_3C\begin{matrix}\nearrow CH . C(OH) \searrow\\\searrow CH_2 . CH_2 \nearrow\end{matrix}CCO_2C_2H_5]$, boiling at 151° (22 mm.), is produced from the interaction of methylene iodide and acetoacetic ester in a form soluble in alkali and a form insoluble in alkali (keto- and hydroxyl ?). The neutral ester is changed by treatment with sodium ethylate in ether into the sodium salt of the ester soluble in alkali. Both esters, when treated with sodium alcoholate and isopropyl iodide, yield—

3,6-*Methylisopropyl-Δ_2-keto-R-hexene-6-carboxylic ester*, boiling at 158° (18 mm.). The corresponding keto-R-hexene (p. 298) (B. **30**, 639) is obtained from this ester by saponification and the splitting-off of carbon dioxide.

2. HYDROAROMATIC DICARBOXYLIC ACIDS.

A. **Hexahydrodicarboxylic Acids.**—These acids, depending upon the position of the carboxyl groups with reference to one another, show the deportment of dialkyl malonic acids, sym. dialkylsuccinic acids, sym. α-dialkylglutaric acids, and sym. α-dialkyladipic acids.

Hexamethylene-1,1-dicarboxylic ester and 2-**Methylhexamethylene-1,1-dicarboxylic ester** have been made by the action of sodium malonic ester upon pentamethylene bromide and methyl-pentamethylene bromide. The free acids, when heated, split off CO_2 and become hexahydrobenzoic acid and hexahydro-o-toluic acid. 2-**Methylhexamethylene-1,1-dicarboxylic Acid,** $CH_2<\begin{matrix}CH_2 . CH(CH_3)\\CH_2 . CH_2 \text{——}\end{matrix}>C(CO_2H)_2$, melts at 147°. *Hexamethylene dicarboxylic acid and its* esters *appear not to have been isolated* as yet (B. **21**, 735; **26**, 2246).

Hexahydrophthalic Acids.—A. Baeyer's theory (B. **23**, R. 577), based upon the spacial representations of van t'Hoff as to the union of the C-atoms, predicts the possibility of geometrically isomeric hexahydrophthalic acids. The latter isomerism is due to the different positions occupied by the carboxyls relatively to the plane of the hexamethylene ring; hence the isomerides are termed *cis* and *trans* forms.

cis-**Hexahydro-o-phthalic Acid,** 1,2-*Hexamethylenedicarboxylic Acid*, $C_6H_{10}(CO_2H)_2$, melts at 192° and its *anhydride* melts at 32° and boils at 145° (18 mm.); the trans-**Hexahydro-o-phthalic Acid** melts at 215° and its *anhydride* at 140°. They are produced together when Δ_1-tetrahydro-o-phthalic acid is reduced. The cis-acid is more soluble in water than the trans-acid. The anhydride of the latter is converted by continuous heating at 210–220° into the anhydride of the cis-acid (A. **258**, 214).

Hexahydro-isophthalic Acids are produced in the reduction of isophthalic acid and when 1,1,3,3-hexamethylenetetracarboxylic acid is heated to 200–220°. The calcium salt of the cis-acid is more sparingly soluble. The *cis-acid*, melting at 162°, when heated *to 180° with hydrochloric acid, changes in part to the trans-acid*, melting *at 188°*. Both acids, with acetyl chloride, yield the *acid anhydride*, melting at 119° (B. **26**, R. 721).

Hexahydroterephthalic Acids result on reducing the hydrobromides of the tetrahydroterephthalic acids in glacial acetic acid with zinc-dust, as well as upon heating hexamethylene-1,1,4,4-tetracarboxylic acid to 200–220°. In the latter case the trans-acid, melting at 200°, predominates. The cis-acid, melting at 161°, is also converted into it when heated with hydrochloric acid to 180°. As far as concerns solubility, these three pairs of hexahydrophthalic acids reduce fumaric and maleïc acids. They are also convertible one into the other in like manner. They have also been distinguished, one from the other, as *maleïnoïd* and *fumaroïd* modifications.

a-Brom-substitution products of these acids have also been prepared from the acid chlorides by treatment with bromine. Brom-substituted hexahydrocarboxylic acids have also been obtained by the addition of hydrogen bromide and bromine to the corresponding tetra- and dihydrodicarboxylic acids.

B. Tetrahydrodicarboxylic Acids, *Tetrahydro-o-phthalic Acids.*—Depending upon the point of double union there are, theoretically speaking, four structurally isomeric bodies. The two modifications in which neither of the two CO_2H-groups are attached to a doubly combined C-atom permit of a stereoisomeric modification each.

Δ_1-**Tetrahydro-o-phthalic Acid,** $\begin{array}{l} CH_2 . CH_2 . C . CO_2H \\ | \qquad\qquad\quad \| \\ CH_2 . CH_2 . C . CO_2H \end{array}$, melting at 120° and its *anhydride* at 74°, is formed when hydropyromellitic acid is distilled (p. 307). Potassium permanganate decomposes it into adipic acid (A. 166, 346; 258, 203).

Δ_2-**Tetrahydro-o-phthalic Acid,** $\begin{array}{l} CH_2 . CH = C . CO_2H \\ | \qquad\qquad\quad | \\ CH_2 - CH_2 - CH . CO_2H \end{array}$, melting at 215° and its anhydride at 78°, has been obtained by the decomposition of *sedanonic acid* (B. 30, 503). It is also formed on boiling the Δ_1-acid with caustic potash, when the double union is shifted, and by the reduction of phthalic acid or $\Delta_{2,6}$-dihydrophthalic acid together with trans-Δ_4-**Tetrahydro-o-phthalic Acid,** $\begin{array}{l} CH - CH_2 - CH . CO_2H \\ \| \qquad\qquad\quad | \\ CH . CH_2 . CH . CO_2H \end{array}$, melting at 216° and its *anhydride* at 140°. Acetyl chloride separates it from the Δ_2-acid. This reagent converts it alone into its corresponding anhydride (A. 258, 211).

cis-Δ_4-**Tetrahydro-o-phthalic Acid** melts at 174°. It is produced when the $\Delta_{2,4}$-dihydro-acid is reduced, as well as from its *anhydride*, melting at 58°. The latter anhydride is formed when the anhydride of the trans-Δ_4-acid is heated (A. 269, 202).

Tetrahydro-terephthalic Acids are theoretically possible in two structurally isomeric forms, depending upon the position of the double union; one of these can occur in two stereoisomeric modifications.

Δ_2-**Tetrahydro-terephthalic Acid,** $CO_2H . CH \langle \begin{array}{l} CH = CH \\ CH_2 - CH_2 \end{array} \rangle CH . CO_2H$, is produced in two isomeric modifications by the reduction of $\Delta_{1,3}$- and $\Delta_{1,5}$-dihydroterephthalic acids. The *trans-acid* melts at about 300°. The *cis-acid* melts at 150°. The latter is much more readily soluble in water than the former. Potassium permanganate oxidizes them to succinic acid. Boiling sodium hydrate changes the two acids, like $\beta\gamma$-hydromuconic acid, into $a\beta$-hydromuconic acid (1, 467).

Δ_1-**Tetrahydro-terephthalic Acid,** $CO_2H . CH \langle \begin{array}{l} CH_2 - CH \\ CH_2 - CH_2 \end{array} \rangle C . CO_2H$, melts beyond 300° and sublimes (A. 258, 7).

C. Dihydrocarboxylic Acids.—*Dihydro-o-phthalic Acids* are possible, according to the position of the double union, in six structurally isomeric forms, one of which can occur in two stereoisomeric modifications.

$\Delta_{1,4}$-**Dihydro-o-phthalic Acid,** $\begin{array}{l} CH . CH_2 . C . CO_2H. \\ \| \qquad\qquad \| \\ CH . CH_2 . C . CO_2H \end{array}$, melting at 153° (its *anhydride* at 134°), is produced on boiling $\Delta_{2,4}$-dihydrophthalic acid with acetic anhydride (A. 269, 204).

$\Delta_{2,4}$ **Dihydro-o-phthalic Acid,** $\begin{array}{l} CH . CH_2 . CH . CO_2H \\ \| \qquad\qquad | \\ CH . CH . C . CO_2H \end{array}$, melting at 179° (its anhydride at 103°), is produced when the acid is acted upon in the cold with acetic anhy-

dride. The acid is produced, further, on boiling $\Delta_{2,6}$-dihydro-o-phthalic acid dihydrobromide with methyl alcoholic potash.

$\Delta_{2,6}$-Dihydro-o-phthalic Acid, $\begin{array}{l} CH_2 . CH : C . CO_2H \\ | \qquad\qquad\quad | \\ CH_2 . CH : C . CO_2H \end{array}$, melts at 215° and its *anhydride* at 83°. The acid results by reducing phthalic anhydride with sodium amalgam in alkaline solution, and by boiling the $\Delta_{2,4}$- and $\Delta_{3,5}$-acid with sodium hydrate (see also B. **27**, 3185).

trans-$\Delta_{3,5}$-Dihydrophthalic Acid, $\begin{array}{l} CH : CH . CH . CO_2H \\ | \qquad\qquad\quad | \\ CH : CH . CH . CO_2H \end{array}$, melting at 210°, is produced by reducing phthalic anhydride with sodium amalgam in acetic acid solution.

cis-$\Delta_{3,5}$-Dihydrophthalic Acid melts at 174°. Its *anhydride*, melting at 99°, is formed when the trans-$\Delta_{3,5}$-acid is acted upon with acetic anhydride.

Dihydroterephthalic Acids.—Depending upon the points of double union, there are four possible structural isomerides. One of these, the $\Delta_{2,5}$-acid, appears in two stereoisomeric forms. All the modifications are known.

$\Delta_{1,3}$-Dihydroterephthalic Acid, $CO_2H . C \begin{array}{l} \diagup CH . CH \diagdown \\ \diagdown CH_2 . CH_2 \diagup \end{array} C . CO_2H$, is produced on digesting a,a_1-dibromhexahydroterephthalic acid and Δ_1 tetrahydroterephthalic acid dibromide with alcoholic potash (A. **258**, 23). The *dimethyl ester* melts at 85°.

$\Delta_{1,4}$-Dihydroterephthalic Acid, $CO_2H . C \begin{array}{l} \diagup CH . CH_2 \diagdown \\ \diagdown CH_2 . CH \diagup \end{array} C . CO_2H$, is formed by reducing terephthalic acid with sodium amalgam, by boiling the isomeric dihydroterephthalic acids with sodium hydrate (A. **251**, 272), and by reducing p-dichlor-$\Delta_{1,4}$-dihydroterephthalic acid with sodium amalgam (B. **22**, 2112).

The *dimethyl ester* melts at 130°.

p-Dichlor-$\Delta_{1,4}$-dihydroterephthalic Acid, $C_8H_6Cl_2O_4$, melts at 272–275° with decomposition. It results upon treating succino-succinic ester with PCl_5 (B. **22**, 2106).

$\Delta_{1,5}$-Dihydroterephthalic Acid results on boiling trans-$\Delta_{2,5}$-dihydroterephthalic acid with sodium hydroxide; the *dimethyl ester* resinifies on exposure to the air (A. **258**, 18).

$\Delta_{2,5}$-Dihydroterephthalic Acids, $CO_2H . CH < \begin{array}{l} CH : CH \\ CH : CH \end{array} > CH . CO_2H$, cis-acid and trans-acid, are formed in the reduction of terephthalic acid. See also $\Delta_{1,5}$-dihydroterephthalic acid. The *trans-diphenyl ester* melts at 146°. The *cis-dimethyl ester* melts at 77° (A. **258**, 17).

D. and E. Oxy- and Ketohydrobenzene Dicarboxylic Acids.—**a-Oxy-hexahydroisophthalic Acid,** $CH_2 \begin{array}{l} \diagup CH_2 - CH_2 \\ \diagdown \\ CO_2H . > CH - CH_2 \end{array} > C < \begin{array}{l} CO_2H \\ OH \end{array}$, is obtained from m-keto-hexahydrobenzoic acid by the action of prussic acid and hydrochloric acid (B. **22**, 2186).

m-Dioxyhexahydroisophthalic Acid, $CH_2 < \begin{array}{l} CH_2 - C(OH) - CO_2H \\ CH_2 - C(OH) - CO_2H \end{array} > CH_2$, melts with decomposition at 217°. Its *anhydride* melts at 175°. The acid is obtained from its nitrile, the product of the addition of prussic acid to dihydroresorcinol (p. 297) (A. **278**, 49).

a,a_1-Dioxyhexahydroterephthalic Acid, $\begin{array}{l} CO_2H \\ HO \end{array} > C < \begin{array}{l} CH_2 - CH_2 \\ CH_2 - CH_2 \end{array} > C < \begin{array}{l} CO_2H \\ OH \end{array}$, is formed when its cyanide, melting with decomposition at 180°, is boiled. This cyanide results by adding prussic acid to p-diketohexamethylene with hydrochloric acid (B. **22**, 2176).

Δ_1-Tetrahydro-2-oxyterephthalic Acid, or *2-Ketohexamethylene-1,4-dicarboxylic Acid*,

$$CO_2H . CH \begin{array}{l} \diagup CH_2 . C(OH) \diagdown \\ \diagdown CH_2 . CH_2 - \diagup \end{array} C . CO_2H, \text{ or } CO_2H . CH \begin{array}{l} \diagup CO - CH_2 \diagdown \\ \diagdown CH_2 - CH_2 \diagup \end{array} CH . CO_2H,$$

results from the reduction of oxyterephthalic acid (p. 243). When heated to 60° with water, it splits off carbon dioxide and becomes m-ketohexahydrobenzoic acid (p. 304),

the oxime of which is obtained from tetrahydro-oxyterephthalic acid by means of hydroxylamine hydrochloride (B. **22**, 2178).

Tetrahydro-dioxyterephthalic Acid—p. 243.

Ketotetrahydrobenzene polycarboxylic esters and m-*diketohexahydrobenzene carboxylic esters* or *hydro-resorcylic esters* have been prepared synthetically in great numbers from 1,5-diketone- and δ-ketone carboxylic esters respectively by the elimination of water or of alcohol. A series of keto-R-hexenes, dihydroresorcinols, tetrahydrobenzenes, dihydrobenzenes, etc., has been built up from these bodies as the starting-out substances (pp. 297, 298).

Succino-succinic Acid, $CO_2H \cdot CH<^{CO \cdot CH_2}_{CH_2 \cdot CO}>CH \cdot CO_2H$, results upon saponifying its diethyl ester with a calculated amount of normal sodium hydroxide, and by treating 2,5-dioxyterephthalic ester with sodium amalgam. The dry acid breaks down into two molecules of carbon dioxide and p-diketohexamethylene when heated to 200° (B. **22**, 2168).

Succino-succinic Diethyl Ester, melting at 126°, is produced by the condensation of two molecules of succinic ester through the agency of potassium, sodium, or sodium ethylate upon succinic ester (A. **211**, 306) or bromacetoacetic ester (A. **245**, 74), as well as by the interaction of silver cyanide and iod-acetoacetic ester (A. **253**, 182), and by the reduction of 2,5-dioxyterephthalic ester with zinc and hydrochloric acid (B. **19**, 432).

Succino-succinic ester behaves like phloroglucin. It also manifests many reactions of a ketone, corresponding to formula I of 2,5-diketohexamethylene carboxylic ester; whereas it also conducts itself like a phenol, corresponding then to formula II of 2,5-dioxydihydroterephthalic ester (B. **24**, 2692):

$$\text{I. } CO_2 \cdot C_2H_5 \cdot CH<^{CO-CH_2}_{CH_2-CO}>CH \cdot CO_2C_2H_5$$

$$\text{II. } CO_2 \cdot C_2H_5 \cdot C\lesssim^{C(OH)-CH_2}_{CH_2-C(OH)}\gtrsim C \cdot CO_2C_2H_5.$$

The ester crystallizes in bright green triclinic prisms or colorless needles. It is insoluble in water, dissolves with difficulty in ether, very readily in alcohol; its solution shows a bright blue fluorescence. Ferric chloride imparts a cherry-red color to it. It dissolves in alkalies with a yellow color, yielding metallic derivatives by the replacement of two hydrogen atoms. It does not unite with phenylisocyanate.

With hydroxylamine (in alkaline or acid solution) succino-succinic ester splits off CO_2 and yields *quinone-dioxime carboxylic ester*, $C_6H_3(N \cdot OH)_2 \cdot CO_2R$, melting at 174° (B. **22**, 1283).

With phenylhydrazine it forms a phenylhydrazine derivative of dihydroterephthalic acid (B. **24**, 2687; **26**, R. 590), while with hydrazine it yields hexahydrobenzo-3,4-dipyrazolon (see this) (B. **27**, 472). Also consult dichlordihydroterephthalic acid.

If succino-succinic ester be saponified by dilute alkalies, with exclusion of air, it yields free

Succino-succinic Dimethyl Ester, melting at 152°.

The following compounds are produced as the result of the interaction of sodium succino-succinic diethyl ester and alkyl iodides (B. **26**, 232):

Diethyl Succino-succinic Ester: cis-body is liquid; trans-body melts at 65°.
Di-n-propyl Succino-succinic Ester: cis-body is liquid; trans-body melts at 86°.
Di-isopropyl Succino-succinic Ester: cis-body is liquid; trans-body melts at 116°.

Methyl-n- and Methylisopropyl Succino-succinic Ester boil at 195-200° (25 mm.); see dihydro-p-cymene, p. 294.

p-Dichlorquinone Dicarboxylic Ester, $C_6Cl_2O_2(CO_2C_2H_5)_2$, melting at 195°, consists of yellowish-green crystals (B. **21**, 1761). When reduced with zinc-dust and glacial acetic acid it becomes **p-Dichlorhydroquinone-dicarboxylic Ester,** $C_6Cl_2H_2O_2(CO_2C_2H_5)_2$, crystallizing in two different forms—colorless needles and yellow-green

plates (B. **20**, 2796; **21**, 1759; **23**, 260). Compare the two forms of 2,5-dioxytere-phthalic ester, p. 243.

p-Dioxy-quinone-dicarboxylic Ester, $C_6O_2(OH)_2(CO_2C_2H_5)_2$, melting at 151°, may be prepared by shaking dichlorhydroquinone-dicarboxylic ester with sodium hydroxide, and by the action of nitrous acid upon dioxy-terephthalic ester (B. **19**, 2385). It crystallizes in pale yellow leaflets and intense greenish-yellow prisms (B. **20**, 1307). Note above, p-dichlorhydroquinone-dicarboxylic ester, and see p. 243. It reacts acid, and forms salts with two equivalents of the metals. It does not form a dioxime with hydroxylamine, but an oxyammonium salt, and with phenylhydrazine a phenylhydrazine salt (B. **22**, 1290). Furthermore, it does not react with phenylcyanate (B. **23**, 265). Boiling hydrochloric acid decomposes the ester into carbon dioxide and dioxy-quinone (p. 170). By the absorption of two atoms of hydrogen (by reduction with sulphurous acid) the ester becomes—

Tetroxy-terephthalic Ester, $C_6(OH)_4(CO_2R_2)$, or **Dioxy-quinone-dihydrocarboxylic Ester**, $C_6H_2(O_2)(OH)_2(CO_2R)_2$. *It crystallizes in golden yellow leaflets* and melts at 178° (B. **20**, 2798). Its alkaline solution oxidizes on exposure to the air (giving up two hydrogen atoms) to dioxy-quinone-dicarboxylic ester; hence it yields the same products with hydroxylamine and phenylhydrazine (B. **22**, 1291). It forms a tetracar-banilido-derivative (B. **23**, 267) with four molecules of phenylcyanate.

1,3,5-Triketohexamethylene Dicarboxylic Ester, $C_6H_4O_3(CO_2C_2H_5)_3$, melting at 101°, results from the condensation of acetone dicarboxylic ester and malonic ester with sodium ethylate (B. **29**, R. 1117).

3. **Hydrobenzene Tricarboxylic Acids.**—This group probably includes **dioxy-phenylacetic dicarboxylic triethyl ester**, $CH_2\!<\!\begin{matrix}CO-CH(CO_2C_2H_5)\\CO-C(CO_2C_2H_5)\end{matrix}\!>\!C.CH_2.CO_2C_2H_5$ or $CO_2C_2H_5CH\!<\!\begin{matrix}CO-CH_2\\CO-C(CO_2C_2H_5)\end{matrix}\!>\!C.CH_2.CO_2C_2H_5$ (pp. 44, 229), and a similarly prepared body—

Phloroglucin Tricarboxylic Ester, $CO_2.C_2H_5.CH\!<\!\begin{matrix}CO-CH(CO_2C_2H_5)\\CO-CH(CO_2C_2H_5)\end{matrix}\!>\!CO$, melting at 104°. It may be formed by the condensation of malonic ester upon heating its sodium compound to 120–145°, or by the action of zinc ethyl. It deports itself quite like succino-succinic ester, dissolves unchanged in alkalies, and is colored a cherry-red by ferric chloride. Acetic anhydride converts it into a *triacetyl derivative*, and with hydroxylamine it yields a *trioxime* (B. **21**, 1766); with phenyl cyanate it forms a tricarb-anilido derivative (B. **23**, 270). Fused with alkalies it forms phloroglucin.

4. **Hydrobenzene-tetracarboxylic Acids.**—Acids having two carboxyl groups attached to the same carbon atom have been obtained synthetically in the action of tri-methylene bromide upon the disodium compound of methylene dimalonic ester, as well as from the interaction of methylene iodide and disodiumtrimethylene dimalonic ester: hexamethylene-1,1,3,3-tetracarboxylic ester, and from n-butanetetracarboxylic ester with ethylene bromide: hexamethylene-1,1,4,4-tetracarboxylic ester (Perkin, Jr.; see p. 20):

$$CH_2\!<\!\begin{matrix}CH_2-\overset{(CO_2C_2H_5)_2}{CNa}\\CH_2-\underset{(CO_2.C_2H_5)_2}{CNa}\end{matrix} + I_2CH_2 = CH_2\!<\!\begin{matrix}CH_2-\overset{(CO_2C_2H_5)_2}{C}\\CH_2-\underset{(CO_2.C_2H_5)_2}{C}\end{matrix}\!>\!CH_2 + 2NaI.$$

1,1,3,3-Hexamethylenetetracarboxylic Acid decomposes at 220° with the elimination of $2CO_2$ into hexahydroisophthalic acid (B. **25**, R. 159, 274).

1,1,4,4-Hexamethylenetetracarboxylic Acid, melting at 152–153°, yields, at more elevated temperatures, both hexahydroterephthalic acids; the trans-acid predominates (p. 302).

Tetra-hydro- and iso-tetra-hydro-pyro-mellitic Acids, $C_6H_2(H_4)(CO_2H)_4$, are obtained by the continued action of sodium amalgam upon the aqueous solution of ammonium pyromellitate. The first results as a gummy mass upon evaporating the ethereal

solution; it is very soluble in water. The second crystallizes with $2H_2O$, loses the same about 120°, melts near 200°, and decomposes into water, carbon dioxide, and Δ_1-tetrahydro-o-phthalic anhydride (p. 303) (A. 258, 205). When heated with sulphuric acid both evolve CO_2 and SO_2 and form trimellitic and isophthalic acids.

Quinone-tetrahydro-tetracarboxylic Ester, or **p-Diketohexamethylene-tetracarboxylic Ester,** $\begin{array}{l}CO_2.C_2H_5.CH-CO-CH.CO_2.C_2H_5\\ \quad\quad\quad\quad\ \ | \quad\quad\quad\quad\quad\ \ |\\ CO_2.C_2H_5.CH-CO-CH.CO_2.C_2H_5\end{array}$, melts at 142–144°, when it is anhydrous. It is formed in the reduction of hydroquinone-tetracarboxylic ester (p. 246), the reduction product arising from quinone-tetracarboxylic ester (p. 246), zinc-dust, and hydrochloric acid in alcoholic solution. It crystallizes from alcohol in *colorless* needles or prisms. Its deportment is perfectly analogous to that of succino-succinic ester. Ferric chloride imparts a cherry-red color to its alcoholic solution. Bromine changes it again to hydroquinone-tetracarboxylic ester (B. 22, R. 289).

Tetrahydroprehnitic Acid, $C_6H_6(CO_2H)_4$, is formed when sodium amalgam acts upon an ammoniacal solution of prehnitic acid (p. 246). It is an amorphous mass, very readily soluble in water. It yields prehnitic and isophthalic acids when it is heated with sulphuric acid.

5. **Hexahydrobenzene-hexacarboxylic Acids.—Hexahydromellitic Acid,** $C_6H_6(COOH)_6$, is produced when sodium amalgam acts upon ammonium mellitate. It is very soluble in water and crystallizes with difficulty. It melts with decomposition when it is heated. Its calcium salt is more easily soluble in cold than in hot water. When heated to 180° with concentrated hydrochloric acid, and also when it is preserved, it passes into isomeric—

Isohexahydromellitic Acid, $C_6H_6(CO_2H)_6$, which crystallizes in large hexagonal prisms. It is precipitated from its salt solutions by hydrochloric acid.

Ring-formation of Hydroaromatic Compounds from Aliphatic Compounds.—The following hydroaromatic bodies have been synthetically prepared from aliphatic compounds:

1. Hexahydrobenzene (p. 292).
2. m-Dihydroisoxylene (p. 294).
3. Pimelin-ketone, Ketohexamethylene, and homologues (p. 296).
4. Trimethylketo-R-hexene or Isoacetophorone (p. 298).
5. Dihydroresorcinol and homologues (p. 296).
6. β-Ketohexamethylenecarboxylic Ester (p. 301).
7. 2-Methyl-1-acetylhexamethylenecarboxylic Ester (p. 301).
8. 3-Methyl-Δ_2-keto-R-hexene-6-carboxylic Ester and homologues (pp. 298, 302, 305).
9. Hexamethylene-1,1-dicarboxylic Ester and homologues (p. 302).
10. m-Diketohexahydrobenzene-carboxylic Ester (p. 305).
11. Succino-succinic Ester (p. 305).
12. Dioxyphenylaceto-dicarboxylic Ester (p. 306).
13. Phloroglucin Tricarboxylic Ester (p. 306).
14. Hexamethylene-1,1,3,3-tetracarboxylic Ester (p. 306).
15. Hexamethylene-1,1,4,4-tetracarboxylic Ester (p. 306).

TERPENES.*

The *volatile* or *ethereal oils*, obtained mostly by the distillation of various plants (chiefly Coniferæ and Citrus species) with steam, more rarely by pressing them out, contain, along with different compounds, certain hydrocarbons having the formula $C_{10}H_{16}$, which are called *Terpenes*. *Isoprene*, C_5H_8, obtained by the distillation of caoutchouc, has the same percentage composition; it is a *hemiterpene*. There are also hydrocarbons

* Fr. Heusler, "Die Terpene." 1896. Verlag von F. Vieweg u. Sohn, Braunschweig.

known having the formula $C_{15}H_{24}$; these are the *sesquiterpenes*, and there are also higher polymerides, $(C_5H_8)x$, the *polyterpenes*.

The "*true terpenes*," $C_{10}H_{16}$, the important and often the chief components of many ethereal oils of great value in perfumery, demand particular attention. They contain one, and some of them probably two carbon rings. They are more or less closely related to cymene or p-isopropyl methyl benzene (p. 56). In recent years terpenes have also come to light which do not have a closed carbon chain; they are distinguished from the true terpenes as *olefine terpenes*.

Their classification and the possibility of distinguishing the individual *true terpenes* are mainly due to the painstaking researches of O. Wallach, who has brought order and system out of this chaotic mass of hydrocarbons of the most varying origin.

The question as to the constitution of the true terpenes has not yet been entirely settled as to any representative of this group of bodies. They can, however, be arranged into two sub-groups.

Camphene, obtained from bornyl chloride, is a terpene. It probably continues to hold the carbon skeleton of camphor (p. 327). *Fenchone* and *pinene* are related to it. These are three cyclic terpenes. They are only capable of adding two univalent atoms or atomic groups. The cyclic terpenes of the *limonene* and *pentene* group are distinguished from the preceding bodies chiefly by their power of adding four univalent atoms. In this class we find hydrocarbons similar to the synthetically prepared p-dihydrocymene (p. 294). These cyclic hydrocarbons of the formula $C_{10}H_{16}$ may be called *hydroaromatic terpenes* in contradistinction to the *camphenes*, $C_{10}H_{16}$. Individual members of both groups are genetically allied to one another by certain transition-reactions. All of the true terpenes are unsaturated hydrocarbons; by the addition of hydrogen they become *hydroterpenes*.

The hydroterpenes give rise to a great number of alcohols and ketones, comprised under the general name *camphor*. In this class are included *menthone*, *mentha camphor*, and *common* or *Japan camphor*, a ketone of dihydrocamphene. The *terpene alcohols* and *terpene ketones*, with their transposition products, attach themselves naturally to the terpenes and their addition products.

Properties.—The true terpenes, when pure, are colorless, strongly refracting liquids. Camphene alone is a solid.

They boil without decomposition at 155–180°. They are very volatile with steam and have a pleasant odor. Many are optically active. Some, indeed, exist in two optically active forms with equal but opposite rotatory power. Dipentene is a racemic terpene.

Deportment.—(1) Some terpenes polymerize very readily. (2) Boiling dilute alcoholic sulphuric acid has rearranged various terpenes into isomeric terpenes. (3) Many are oxidized by the oxygen of the air; they then manifest a tendency to resinify (see B. 29, R. 658). The formation of benzene derivatives by oxidizing terpenes is very important. Thus, turpentine oil with iodine yields cymene; with nitric acid, p toluic acid and terephthalic acid. (4) The addition-reactions have already been pointed to as a means of classifying the terpenes. The terpenes capable of adding four hydrogen atoms are in all probability dihydrocymenes (see above). For the constitution of the camphene adding but two hydrogen atoms consult p. 327. (5) The addition of chlorine and bromine, as well as hydrogen halides, in glacial acetic acid at low temperatures gives rise to haloid hydroterpenes. Conversely, when the hydrogen halide addition-products are heated with sodium acetate in glacial acetic acid, or when heated with bases like aniline, the terpenes are regenerated. It is by means of these haloid bodies that the transition from

the terpenes into camphor alcohols can be realized. (6) Nitrosyl chloride, NOCl (Tilden), or an alkyl nitrite, glacial acetic acid, and hydrochloric acid acting upon terpenes give rise to well-defined terpene nitroso-chlorides. These form terpene nitrolamines with primary and secondary bases, or, by splitting off hydrochloric acid, they become nitroso terpenes. v. Baeyer (B. **28**, 648; **29**, 10) contends that these nitrosochlorides are frequently to be regarded as bimolecular, and better as bisnitrosochlorides. (7 *a*) Several terpenes unite with N_2O_4, forming nitrosates, $C_{10}H_{16}(NO).O.NO_2$, (*b*) and with N_2O_3, yield nitrosites, $C_{10}H_{16}(NO).O.NO$. See B. **29**, 695, for the addition of trichloracetic acid to the terpenes.

Nomenclature.—Baeyer, observing the "Geneva nomenclature," suggested that the cyclic terpenes containing the same carbon skeleton as p-cymene, the dihydro-p-cymenes, be called *Terpadiënes*; then the tetrahydrocymenes would be *terpenes* and hexahydrocymene *terpan*. Camphene would retain its name, but dihydrocamphene would receive the name *camphan*; consequently, the terpenes can be divided into the *terpan* and *camphan* groups. To obtain names for the terpenes which would be designated, according to this suggestion, as terpadiënes, Wagner calls hexahydrocymene *menthan*, the tetrahydrocymenes *menthenes*, and the dihydrocymenes or terpenes *menthadiënes* (B. **27**, 1636 Anm.).

The terpenes will, therefore, be discussed in three groups:
A. Olefinic Terpene- or Terpenogen Group.
B. Terpan or Menthan Group.
C. Camphan Group.
The alcohols and ketones, the so-called *camphors*, attach themselves to the hydrocarbons of each group.

A. OLEFINIC TERPENE- OR TERPENOGEN GROUP.

Many olefine hydrocarbons, alcohols, aldehydes, and acids with open carbon chain are included under this designation. They occur in ethereal oils, or in the transposition products obtained from the latter. They are distinguished chiefly by the fact that they, as a rule, are easily converted into hydroaromatic, terpene-like, or aromatic substances.

1. **Olefinic Terpenes: Myrcene**, $C_{10}H_{16}$, boiling at 67° (20 mm.), sp. gravity 0.8025 (15°), $n_D = 1.4673$, occurs with l-phellandrene and the aromatic phenols of the cinnamic series in bay-oil. It can take up six atoms of bromine, and by the addition of hydrogen becomes linalool. **Anhydrogeraniol**, $C_{10}H_{16}$, boiling at 172–176°, sp. gr. 0.8232 (20°), $n_D = 1.4835$, and obtained by heating geraniol with potassium sulphate to 170°, can also take up six bromine atoms (B. **24**, 682). **Linaloolene**, $C_{10}H_{18}$, boils at 165–168°. Its sp. gravity is 0.7882 (20°), $n_D = 1.455$. It is formed in the reduction of linalool (B. **27**, 2520).

Isoprene, C_5H_8, boiling at 37°, must be considered under the olefinic terpenes or terpenogens. It is a distillation product from caoutchouc (p. 311). It very probably consists in the main of *methyldivinyl*, $\begin{matrix}CH_3\\CH_2\end{matrix}\!\!>C-C=CH_2$. It can take up two molecules of hydrogen bromide, forming dimethyl-trimethylene bromide. It polymerizes very readily to dipentene (p. 311) (J. pr. Ch. [2], **55**, 1):

$$2\,\begin{matrix}CH_3\\CH_2\end{matrix}\!\!>C-CH=CH_2 \longrightarrow \begin{matrix}CH_3\\CH_2\end{matrix}\!\!>C-CH\!\!<\!\begin{matrix}CH_2-CH\\CH_2-CH_2\end{matrix}\!\!>CCH_3.$$

2. **Olefinic Terpene Alcohols: Rhodinol**, $C_{10}H_{20}O$, boiling at 113–114° (15 mm.), occurs, together with geraniol, in different rose, geranium, and pelargonium oils. Very probably it must be viewed as the optically active lævorotatory alcohol, corresponding to citronellal: l-*citronellol*, $(CH_3)_2.C:CH.CH_2.CH_2.C(CH_3)H.CH_2.CH_2OH$ (B. **29**, 923 ff.; **30**, 33; compare B. **29**, R. 785).

Geraniol, $C_{10}H_{18}O = (CH_3)_2C:CH.CH_2.CH_2.C(CH_3):CH.CH_2OH$, boiling at 120–122° (17 mm.) constitutes the alcoholic constituent of geranium oil, rose oil, pelargonium oil, etc. (B. **29**, 785). It is optically inactive, and bears the same relation to rhodinol that citral sustains to citronellal.

l-Linalool, $C_{10}H_{18}O = (CH_3)_2C:CH.CH_2.CH_2.C(CH_3)OH.CH:CH_2$, boiling at 197–199°, sp. gr. 0.8702 (20°), $n_D = 1.4695$, is found in oil of lavender, bergamot, limet, and origanum. d-**Linalool**, *coriandrol*, occurs in the oil of coriander. Dilute sulphuric acid converts the linalool with ease into inactive *terpine hydrate* (p. 314); this conversion is made with greater difficulty with geraniol (B. **28**, 2137).

The constitution of these bodies, as well as that of the corresponding aldehydes and acids, has been mainly deduced from their conversion into *methyl heptenone*, $(CH_3)_2C:CH.CH_2.CH_2.CO.CH_3$, which has been previously described. Again, this methyl heptenone has been employed in the synthesis of certain bodies belonging in this group. Thus, by condensation with zinc and allyl iodide it yields **homolinalool**, $(CH_3)_2C:CH.CH_2.CH_2C(CH_3)OH.CH_2.CH:CH_2$, boiling at 102–104° (14 mm.) (B. **29**, 693).

Another series of olefinic terpene alcohols—*e. g.*, *licareol*, *réuniol*, *ylangol*—has been prepared from various ethereal oils. Their constitution has not yet been determined; probably they are identical with the compounds just described, or they are closely related to them (B. **27**, R. 505, 751; **28**, R. 67).

3. **Olefinic Terpene Aldehydes: Citronellal** (Rhodinal?) (B. **29**, R. 352), $C_{10}H_{18}O = (CH_3)_2C:CH.CH_2.CH_2.C(CH_3)H.CH_2.CHO$, boiling at 103–105° (25 mm.), is optically dextrorotatory. It is found in citronella oil, in the oil from *Eucalyptus maculata, var. citriodora*, etc. (B. **29**, 904). Acetic anhydride condenses it to *isopulegol*, a terpene alcohol very similar to, yet not identical with, pulegol, a reduction product obtained from pulegon (p. 320) (B. **30**, 22). It changes to d-citronellol (see this) upon reduction.

Citrel, *Geranial*, $C_{10}H_{16}O = (CH_3)_2C:CH.CH_2.CH_2.C(CH_3):CH.CHO$, boiling at 224–228°, is formed in the oxidation of geraniol. It is also present in the oil of lemons. When condensed by potassium bisulphate, HI, acetic acid, etc., the double linking is displaced and cymene results. When citral is condensed with acetone it yields **Pseudoionone**, $(CH_3)_2C:CH.CH_2.CH_2C(CH_3):CHCH:CHCOCH_3$, boiling at 143–145°. On heating this with dilute sulphuric acid it changes to **ionone**, an hydroaromatic ketone (B. **27**, R. 768).

4. **Olefinic Terpenic Acids: Citronellic Acid** (*Rhodinic Acid?*) (B. **29**, R. 352), $(CH_3)_2C:CH.CH_2.CH_2C(CH_3)H:CH_2.COOH$, boiling at 143.5° (10 mm.), is obtained from its nitrile, formed in the dehydration of citronella aldoxime, or by oxidizing citronellal (B. **29**, 905).

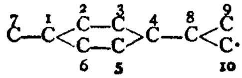
Geranic Acid, $(CH_3)_2C:CH.CH_2.CH_2C(CH_3):CH.COOH$, boiling at 153° (13 mm.), is also obtained from citral. It has also been synthetically prepared from methyl heptenone (see above) and iodacetic ester (B. **29**, R. 222). Sulphuric acid converts it into isomeric hydroaromatic *isogeranic acid* (p. 301).

B. TERPAN OR MENTHAN GROUP.

1. Hydrocarbons. (*a*) Limonene or Dipentene Group.

The terpenes of this group combine with four atoms of bromine or with two molecules of halogen hydride, but not with N_2O_3. They very probably are dihydrocymenes. One of the dihydro-p-cymenes has been synthesized (p. 294), but as yet has been too imperfectly studied to compare it with the appended terpenes.

To indicate the constitution of the dihydrocymenes the carbon atoms are provided with numbers:



The dihydrocymene of the formula $CH_3 . C \langle {CH - CH_2 \atop CH_2 - CH_2} \rangle C = C(CH_3)_2$, would then be termed $\Delta_{1,4}(8)$-Terpadiëne; and dihydrocymene,

$CH_3 . C \langle {CH - CH_2 \atop CH_2 - CH} \rangle C . CH(CH_3)_2$, would be $\Delta_{1,4}$-terpadiëne (B. **27**, 436).

Limonene, $C_{10}H_{16}$, is known in three modifications—d-limonene, l-limonene, and [d + l] limonene or dipentene.

d-Limonene, *Citrene, Hesperidene, Carvene*, together with pinene, is among the most widely distributed terpenes. It is present in the oil obtained from the shell of *Citrus aurantium*, in citrone oil, in the oil of bergamot, in oil of dill, in oil of celery, etc. It boils at 175°, $[\alpha]_D = + 106.8°$. **l-Limonene** occurs in the oil of pine-needles, in oil of fir, and in oil of peppermint. It boils at 175°; $[\alpha]_D = - 105°$.

Both limonenes are liquids with an agreeable lemon-like odor. Their sp. gravity equals 0.846 (20°). They differ from each other, as do their derivatives, almost entirely by their opposite rotatory power (A. **252**, 144). The two active limonenes combine with dry bromine to *tetrabromides*, melting at 104°, and having equally large but opposite rotatory power of about $[\alpha]_D = 73°$. Dry hydrochloric acid gas converts them into optically active *limonene hydrochlorides*, while the moist haloid acids change the optically active limonenes to addition products of [d + l]-limonene or dipentene. When the optically active limonenes are exposed to elevated temperatures they become dipentenes.

The nitroso-chlorides of the limonenes deserve particular attention (B. **28**, 1308; compare also B. **29**, 10). d-Limonene forms two chemically identical nitrosochlorides, with, however, different physical properties:

α-**d-Limonene-nitroso-chloride** melts at 103°; $[\alpha]_D = + 313.4°$.
β-**d-Limonene-nitroso-chloride** " " 105°; $[\alpha]_D = + 204.3°$.

d-Carvoxime (p. 320) is formed when these bodies are heated with alcoholic potash. d-Limonene, upon oxidation, yields limonetrite (p. 316).

l-Limonene also forms two differently rotating nitroso-chlorides, which, by loss of hydrochloric acid, rearrange themselves into l-carvoxime.

[d + l]-Limonene, Dipentene, Cinene,

$CH_3 . C \langle {CH - CH_2 \atop CH_2 - CH_2} \rangle CH . C \langle {CH_2 \atop CH_3} $ (?) (p. 315) (B. **28**, 2145; **29**, 4), boils at 175°. It is associated with cineol in *Oleum cinæ*. It is produced by heating d-limonene, l-limonene, pinene, and camphene to 250–300°; it is, therefore, present in the Russian and Swedish turpentine oil, obtained by application of great heat. It is derived further by the distillation of caoutchouc, and the polymerization of the **isoprene**, C_5H_8, formed simultaneously (A. **227**, 295). It is also produced on mixing equally large quantities of d- and l-limonenes, as well as when pinene is boiled with alcoholic sulphuric acid. It forms, too, on withdrawing water from linalool, terpine hydrate, terpineol, and cineol. It may be prepared pure by heating its hydrochloride with aniline or sodium acetate in glacial acetic acid solution (A. **245**, 197; B. **26**, R. 319).

Pure dipentene is a liquid with an agreeable lemon-like odor. Its sp. gr. is 0.853, and it is optically inactive.

Although more stable than most of the other terpenes, it can yet be changed into the isomeric terpinene by alcoholic sulphuric acid, or hydrochloric acid. It is oxidized to p-cymene by concentrated sulphuric acid or phosphorus pentasulphide.

The derivatives of dipentene can be obtained not only from the dipentenes, but also by mixing the corresponding derivatives of dextro- and lævo-limonene.

Dipentene Dihydrochloride, $C_{10}H_{16} . 2HCl$, boils at 119° (10 mm.) and melts at 50°.

The trans-*dipentene dihydrobromide*, $C_{10}H_{16}.2HBr$, from d-limonene, dipentene, terpine, and cineol with hydrobromic acid, melts at 64°.

cis-Dipentene dihydro-bromide, $C_{10}H_{16}.2HBr$, melting at 37°, results from the action of HBr upon a well-cooled solution of cineol in glacial acetic acid; see also cis-terpine (B. **26**, 2864).

Tetrahydro-dipentene Tribromide, *Tribromterpan*, $C_{10}H_{17}Br_3$, is derived from trans-dipentenedihydrobromide by the action of bromine upon the glacial acetic acid solution (A. **264**, 25).

Dipentene Tetrabromide, $C_{10}H_{16}.Br_4$, melts at 124° (A. **281**, 140).

Dipentene Dihydro-iodide, $C_{10}H_{16}.2HI$, melts at 77–79° (A. **239**, 13).

Dipentene Nitrosochloride, $C_{10}H_{16}(NO)Cl$, melts at 102°; see carvoxime, p. 321 (A. **270**, 175).

Terpinolene, $CH_3.C\left\langle\begin{matrix}CH-CH_2\\CH_2-CH_2\end{matrix}\right\rangle C=C\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$ (?), melting at 75° (14 mm.), has not yet been observed in ethereal oils. It is produced when terpine hydrate, terpineol, and cineol are boiled with dilute sulphuric acid, and by heating pinene with the concentrated acid. Boiling oxalic acid also liberates it from the terpineol melting at 35° (A. **275**, 106). The *dibromide*, $C_{10}H_{16}Br_2$, melts at 70° (B. **27**, 447). The *tetrabromide*, $C_{10}H_{16}Br_4$, is a solid, melting at 116°.

Sylvestrene, $C_{10}H_{16}$, boiling at 176°, occurs in Swedish and Russian turpentine oil. It is optically dextro-rotatory; $[\alpha]_D = +66.32°$ (A. **252**, 149). Sulphuric acid imparts an intense blue color to its solutions in anhydrous acetic acid (or in acetic anhydride). Carvestrene and dihydrobenzene show a like behavior (p. 294), while other terpenes under similar conditions exhibit a red to reddish-yellow coloration. It is one of the most stable terpenes. The *tetrabromide*, $C_{10}H_{16}Br$, melts at 135°. The *dihydrochloride*, $C_{10}H_{18}Cl_2$, melts at 72°, the *dihydrobromide* at 72°, and the *dihydroiodide* at 67°. The *nitrosochloride*, $C_{10}H_{16}(NO)Cl$, melts at 107° (A. **252**, 150).

Carvestrene, $C_{10}H_{16}$, boiling at 178°, results from the distillation of carylamine hydrochloride. It is probably the optically inactive isomeride corresponding to sylvestrene (B. **27**, 3485). Blue coloration, see sylvestrene. The *dihydrochloride* melts at 52°, and the *dihydrobromide* at 48–50°.

Thujen, *Tanacetene*, $C_{10}H_{16}$, from thujonamine hydrochloride, boils at 172–175° (760 mm.), 60–63° (14 mm.); sp. gr. 0.840, $n_D = +1.476$ (20°) (A. **286**, 99).

(*b*) **Terpinenes and Phellandrene**, $C_{10}H_{16}$.—Both are distinguished from the terpenes of the limonene or dipentene groups by the fact that they do not yield tangible derivatives either with bromine or the haloid acids. However, they do form nitrosites with N_2O_3.

Terpinene, $C_{10}H_{16}$, boiling at 179–181°, occurs in cardamom oil. It results on boiling dipentene, terpine, phellandrene, cineol, terpineol, or dihydrocarveol with dilute alcoholic sulphuric acid, and when pinene is shaken with a little concentrated sulphuric acid. It is characterized by its stability toward dilute mineral acids. Its production together with dipentene, when formic acid acts upon linalool, is very noteworthy. It is the most stable of all the terpenes, and is not changed into any other terpene (A. **239**, 38). Terpinene is optically inactive; it has an odor like that of cymene. Nitrous acid converts it into **Terpinene Nitrosite**, $C_{10}H_{16}(NO)O.NO$ or $C_{10}H_{15}(N.OH).O.NO$, melting at 155°, and yielding nitrolamines with bases. Ammonia converts it into *terpinene nitrolamine*, $C_{10}H_{15}(N.OH).NH_2$, melting at 118° (A. **241**, 320).

Phellandrene, $C_{10}H_{16}$, is known in two optically active forms. Both boil at 170°, and have not yet been obtained in a pure condition. They may be classed with the most unstable terpenes. d-*Phellandrene* occurs in the oil of water fennel, *Phellandrium aquaticum*, etc. (A. **246**, 233). **l-Phellandrene** is found in Australian eucalyptus oil from *Eucalyptus amygdalina*, etc.

d-Phellandrene Nitrosite and l-Phellandrene Nitrosite, $C_{10}H_{16}(NO)O.NO$, melt at 105°. The d-nitrosite is lævorotatory, $[\alpha]_D = -183.20°$, while the l-nitrosite is dextro-rotatory. Metallic sodium and alcohol reduce these nitrosites to ketones, $C_{10}H_{18}O$, which have proved to be d- and l-*tetrahydrocarbons*, inasmuch as they form by their union a racemic tetrahydrocarvone identical with the one prepared in another manner (p. 318) (A. **287**, 371).

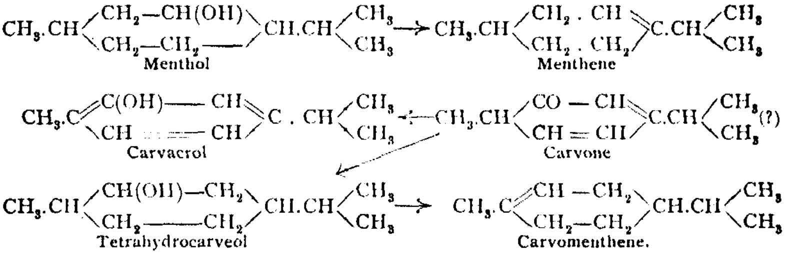
(*c*) **Hydroterpenes.**—Hydrocarbons derived from menthol and tetrahydrocarveol as starting-out substances, and containing two to four atoms more of hydrogen than the preceding bodies, bear close kinship to the latter. The two alcohols just mentioned are derived in such a manner from hexahydro-p-cymene that in both of them there are present secondary ring-alcohols of this hydrocarbon. When they lose water, menthene and carvomenthene are produced. By reducing menthol with HI, or menthyl chloride with sodium and alcohol (B. **29**, 317), a hydrocarbon was obtained, which probably is—

Hexahydrocymene, *Menthonaphthene*, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH\,.\,CH<\begin{matrix}CH_2\,.\,CH_2\\CH_2\,.\,CH_2\end{matrix}>CH\,.\,CH_3$, boiling at 169°. Its specific gravity equals 0.8066 (0°). The hexahydrocymene obtained in the reduction of terpine hydrate (B. **23**, R. 433) and from resin oil is identical with this hydrocarbon.

Tetrahydro-p-cymenes are the two hydrocarbons—

Carvomenthene, $C_{10}H_{18}$, boiling at 175°, and **Menthene**, *Menthomenthene*, $C_{10}H_{18}$, boiling at 167°, with sp. gr. 0.806 (20°) or 0.814 (20°). The latter is best made by acting with potassium phenolate upon menthyl chloride (B. **29**, 1843). See B. **29**, 11, for the *nitroso-chlorides*.

The constitution of the two hydrocarbons follows from their relation to carvacrol and menthol. Carvacrol (p. 145) readily results from a rearrangement of carvone (constitution, compare p. 320), which upon reduction yields tetrahydrocarveol (p. 314), with which menthol is isomeric. The constitution of menthol, on the other hand, is proved by conversion of the corresponding ketone, menthone (p. 318), into 3-chlorcymene and thymol. By removing water from these alcohols, or hydrogen chloride from their chlorides, two different tetrahydrocymenes were formed:



When oxidized with potassium permanganate menthene yields (1) menthene glycol (p. 315), (2) a keto-alcohol boiling at 105° (13.5 mm.), and (3) the fatty acids arising from menthone (B. **27**, 1636).

2. ALCOHOLS OF THE TERPAN OR MENTHAN GROUP.

I (*a*) **Monacid Menthan Alcohols.**—Hexahydro-p-cymene yields the isomeric menthols.

Secondary Menthols.—l-**Menthol**, *Mentha Camphor*, *Oxyhexahydrocymene*, *5-Methyl-2 isopropylhexahydrophenol*,

$CH_3\,.\,CH<\begin{matrix}CH_2\,.\,CH(OH)\\CH_2\,.\,CH_2\end{matrix}>CH\,.\,CH(CH_3)_2$ (see above), melting at 42° and boiling at 212°. It is the chief constituent of peppermint oil (from *Mentha piperita*). It is formed in the reduction of menthone (J. pr. Ch. [2], **55**, 14) and is oxidized by chromic acid to l-menthone (p. 318). By the exit of water it yields menthene (see above), and by reduction hexahydrocymene results (above). Potassium permanganate converts it into

oxomenthylic acid, $CH_3.CH\begin{matrix}\diagup CH_2.CO_2H \\ \diagdown CH_2.CH_2\diagup\end{matrix}CO.CH.(CH_3)_2$, boiling at 174° (15 mm.) (A. **289**, 362), and *β-pimelic acid* or *β-methyl adipic acid*, $CH_3.CH\begin{matrix}\diagup CH_2.CO_2H\diagdown \\ \diagdown CH_2.CH_2\diagup\end{matrix}CO_2H$, melting at 89° (B. **27**, 1818). The speed of ester formation would indicate menthol to be a secondary alcohol.

Menthyl Chloride, $C_{10}H_{19}Cl$, boils at 204°. The *ethyl ether* boils at 212°, and the *benzoyl ester* melts at 54°.

Tetrahydrocarveol, $CH_3.CH<\begin{matrix}CH(OH)-CH_2 \\ CH_2\text{———}CH_2\end{matrix}>CH.CH(CH_3)_2$, isomeric with menthol, is a thick oil, volatile without decomposition. It is formed when tetrahydrocarvone and carvenone (p. 319) are reduced in moist ethereal solution with metallic sodium. Its genetic connection with carvacrol (see above) would indicate its constitution.

Thujamenthol, *Bihydroisothujol*, $C_{10}H_{19}.OH$, boiling at 211–212°, with sp. gr. 0.9015, $n_D = 1.4636$ (20°) (B. **28**, 1958), results from the reduction of isothujone. Although carvenone and isothujone both yield carvacrol with ferric chloride, they yet form different hexahydromonoxycymenes, in which the OH-group should occupy the same position.

Tertiary menthols are produced when their hydriodic acid esters, addition products of HI and menthene by means of carvomenthene, are treated with silver acetate, and the resulting acetates then saponified (see also B. **29**, 1844).

Tertiary Menthol, $CH_3.CH<\begin{matrix}CH_2-CH_2 \\ CH_2-CH_2\end{matrix}>C(OH).CH(CH_3)_2$, boiling at 100° (20 mm.), has a faint peppermint-like odor.

Tertiary Carvomenthol, $CH_3C(OH)<\begin{matrix}CH_2-CH_2 \\ CH_2-CH_2\end{matrix}>CH.CH(CH_3)_2$, boils at 96–100° (17 mm.).

(*b*) **Diacid Alcohols.**—In this group are the two terpines, cis-terpine and trans-terpine, corresponding to the cis- and trans-dipentenedihydrobromides, with which they are intimately related. At present the following formulas are assigned them (see B. **29**, 5):

$$\begin{matrix}CH_3 \\ HO\end{matrix}>C<\begin{matrix}CH_2-CH_2 \\ CH_2-CH_2\end{matrix}>C<\begin{matrix}H \\ C(CH_3)_2OH\end{matrix} \qquad \begin{matrix}HO \\ CH_3\end{matrix}>C<\begin{matrix}CH_2-CH_2 \\ CH_2-CH_2\end{matrix}>C<\begin{matrix}H \\ C(CH_3)_2OH.\end{matrix}$$

cis-Terpine trans-Terpine.

These are in harmony with the oxidation of terpine hydrate to terebic acid (p. 324), as well as with its formation from linalool (p. 310). Cineol is to be regarded as the oxide corresponding to the *cis*-terpine.

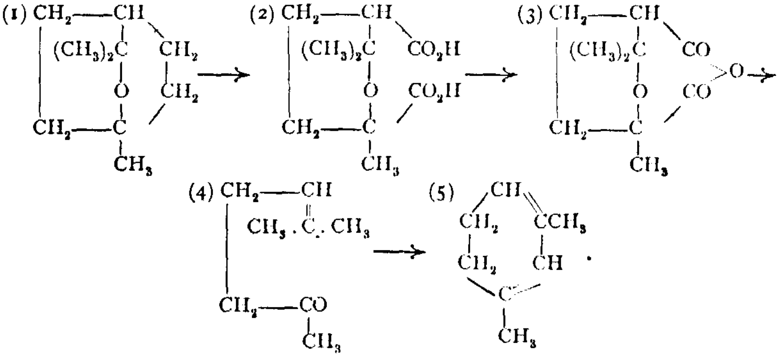
Terpine, cis-*Terpine*, $C_{10}H_{18}(OH)_2$, melting at 104° and boiling at 258°, readily parts with water and becomes *terpine hydrate*, $C_{10}H_{18}(OH)_2 + H_2O$, melting at 117°, from which it is prepared by protracted heating to 100°. Terpine corresponds to cis-dipentenedihydrobromide (p. 311), from which it can be obtained by treatment with silver acetate in glacial acetic acid, and saponifying the resulting diacetyl derivative with alcoholic potash. Terpine hydrate is also produced if turpentine oil is allowed to stand with dilute nitric acid and alcohol (A. **227**, 284), as well as from pinene (p. 322), dipentene, and d-limonene with dilute acids. It forms, furthermore, on bringing dipentene and d-limonene dihydrochloride in contact with water, and when terpineol (p. 316) and cineol are acted upon with dilute acids.

The haloid acids convert terpine hydrate into the cis- and trans-dihydrohalides of dipentene. When boiled with dilute acids it passes into terpineols (B. **27**, 443, 815), cineol, dipentene, terpines, and terpinolenes.

trans-Terpine, $C_{10}H_{18}(OH)_2$, melting at 156–158° and boiling at 263–265°, is formed

from trans-dipentenedihydrobromide (see cis-terpine), into which it finally reverts upon treatment with hydrogen bromide. It does not combine with water of crystallization.

Cineol, $C_{10}H_{18}O$, boiling at 176°, with sp. gr. 0.923 (16°), n_D = 1.4559, is a liquid with a camphor-like odor. It occurs in many ethereal oils, in *Oleum cinæ*, the worm-seed oil of *Artemisia cina*, cajeput oil, eucalyptus oil, rosemary oil, etc. Hydrochloric acid gas conducted into a petroleum ether solution of cineol precipitates an unstable addition product, $C_{10}H_{18}O.HCl$ (?), which water resolves into its components, and which serves for the separation of cineol. In glacial acetic acid solution the haloid acids change cineol into dipentene dihydro-halides. At low temperatures hydrogen bromide produces cis-dipentenedihydrobromide (p. 312). P_2S_5 converts cineol into cymene. Potassium permanganate oxidizes cineol (1) into cineolic acid (2), the anhydride (3) of which yields, upon distillation, methylhexylene ketone or methyl heptenone (4) (constitution, p. 310), while the latter may be arranged to m-dihydroisoxylene (5) (p. 294). This series of reactions is shown in the following diagram:

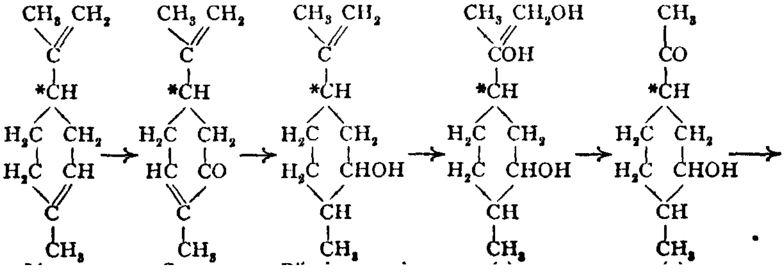


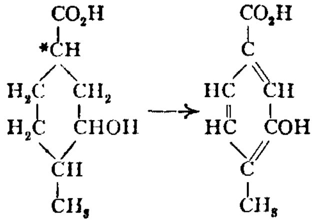
Cineolic Acid melts at 196–197° with decomposition; its *anhydride* melts at 78° and boils at 157° (13 mm.).

Menthene Glycol, $C_{10}H_{18}(OH)_2$, melting at 77° and boiling at 130° (13 mm.), results when menthene is oxidized with potassium permanganate (B. 27, 1636).

(*c*) **Triacid Menthan Alcohols** have been obtained by oxidizing menthene alcohols with potassium permanganate.

1. **Trioxyhexahydrocymene**, $C_{10}H_{17}[2,8,9](OH)_3$ (1), from dihydrocarveol (see below), is a syrup, and with dilute sulphuric acid yields an indifferent oxide, $C_{10}H_{18}O$, boiling at 196–199° (A. 277, 152), while upon oxidation with chromic acid it forms a ketone-alcohol: 5-*acetylhexahydro-o-cresol*, melting at 58° (2), which upon further oxidation changes to *hexahydro*-m-*oxy*-p-*toluic acid*, melting at 153° (3). The constitution of this last acid is evident from its conversion by bromine into m-*oxy*-p-*toluic acid*, melting at 203° (4). These experiments give rise to the constitution formulas (B. 28, 2141):





(3) (4)

2. **Trioxyhexahydrocymene, Dioxyterpineol,** $C_{10}H_{17}(OH)_3$, melting at 121°, formed from the terpineol melting at 35°, passes into carvenone (p. 319) when it is acted upon with dilute sulphuric acid (A. **277**, 122).

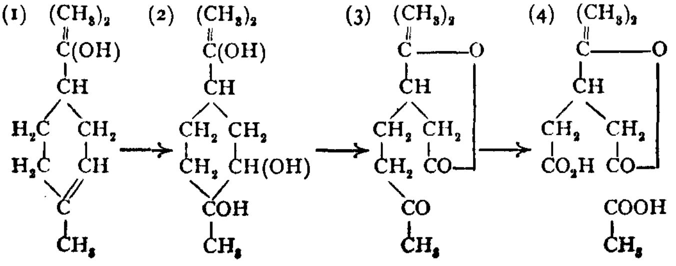
3. *Trioxyhexahydrocymene*, $C_{10}H_{17}[1,4,8](OH)_3 + 3H_2O$, melts in the anhydrous state at 110–112° and boils at 200° (20 mm.). It is formed from $\Delta_{4,8}$-terpineol (B. **28**, 2296).

(*d*) **Tetracid Menthan Alcohols.**—When d-limonene is oxidized it yields **Limonetrite,** $C_{10}H_{16}(OH)_4$, melting at 192° (B. **23**, 2315). This is a sweet-tasting body belonging to this class of compounds. Its constitution is variously considered, depending upon the views held in regard to the point of double union in limonene (B. **28**, 2149).

II. **Menthene Alcohols,** $C_{10}H_{17}OH$, when oxidized with potassium permanganate, yield triacid alcohols.

The reduction of the ketones, carvone, eucarvone (p. 321), and thujone (p. 319), or tanacetone, gives rise to three different alcohols: $C_{10}H_{17}.OH$: (1) **Dihydrocarveol,** boiling at 224° (760 mm.), 112° (14 mm.), with sp. gr. 0.927 (27°) n_D = 1.48168, is optically active, and has an agreeable odor, recalling that of the terpineols; (2) **Dihydroeucarveol** boils at 109° (21 mm.); (3) **Thujyl Alcohol,** *Tanacetyl Alcohol*, boils at 92.5° (13 mm.). Its sp. gr. equals 0.9249, with n_D = 1.4635.

Terpineols: Terpineol, $CH_3.C\begin{matrix}\diagup CH - CH_2 \diagdown \\ \diagdown CH_2 - CH_2 \diagup\end{matrix}CH.C(OH)(CH_3)_2$, melting at 35°, is formed from terpine hydrate (p. 314) by the withdrawal of two molecules of water (A. **275**, 104). It combines very readily with nitrosyl chloride. When hydrogen chloride is withdrawn from this body an *oxyoxime*, melting at 134°, is produced. Boiling dilute acids change it to carvacrol and carvone (B. **29**, R. 587). Hence it follows that in terpineol and carvone the carbon atoms are similarly grouped. Terpineol nitrosochloride and limonene nitrosochloride are correspondingly constituted (p. 311) (B. **29**, 9). Potassium permanganate oxidizes terpineol (1) into trioxyhexahydrocymene, melting at 121° (2), while with chromic acid it yields a ketone-lactone, homoterpenylic acid methyl ketone, $C_{10}H_{16}O_3$ (3), which, under the influence of potassium permanganate, breaks down into acetic acid and terpenylic acid (4) (p. 324). Therefore, in terpineol melting at 35°, the OH-group probably is in union with carbon atom 8 (B. **28**, 1773, 1779):



When terpineol is heated with potassium bisulphate it changes to *dipentene*, and when boiled with oxalic acid to *terpinolene* (p. 312) (A. 275, 104).

The same constitution has been recently assigned to an optically active *terpineol* boiling at 215°, which has been made from d-limonene hydrochloride; it has the odor both of the mayflower and of lilac (B. 28, 2189).

Terpineol, $CH_3C(OH)<\begin{smallmatrix}CH_2-CH_2\\CH_2-CH_2\end{smallmatrix}>C=C(CH_3)_2$, melts at 69°. Its acetate results on treating tribromterpan or tetrahydrodipentene tribromide (p. 311) with glacial acetic acid and zinc-dust. HBr converts it into dipentene dihydrobromide, and with NOCl a *blue* nitrosochloride, just as tetramethylethylene does. Consequently it probably also contains a tertiary-tertiary double union. In addition, its OH-group must be in such a position that dipentenedihydrobromide can be produced with hydrogen bromide.

III. **Menthadiëne Alcohols.—Carveol Methyl Ether**, $C_{10}H_{15}OCH_3$, boiling at 208–212°, with sp. gr. 0.9065, $n_D = 1.47586$ (18°), represents the methyl ether of such an alcohol. It is formed in the action of sodium upon the alcoholic solution of limonene tetrabromide. Chromic acid oxidizes it to inactive carvone (A. 281, 140). **Isocarveol**, $C_{10}H_{15}OH$, is obtained from pinylamine (A. 279, 387).

3. BASES OF THE TERPAN OR MENTHAN GROUP.

Menthan bases have been obtained by the reduction of the oximes of the menthan ketones with sodium and alcohol, or upon heating the ketones with ammonium carbonate.

R-**Menthylamine** and L-**Menthylamine**,

$$CH_3.CH<\begin{smallmatrix}CH_2-CH\\CH_2-CH_2\end{smallmatrix}\overset{NH_2}{\diagup}>CH.CH(CH_3)_2,$$

boiling at 205°, have an unpleasant odor and attract CO_2 from the air. The bases have opposite, but *unequal*, rotatory power; the same is true of their derivatives (A. 276, 299). They can be separated by means of their formyl compounds, both of which are formed on heating menthene with ammonium formate. R-*Formylmenthylamine*, melting at 117°, dissolves with more difficulty. L-*Formylmenthylamine* melts at 102°. L-menthylamine can also be obtained from l-menthoxime.

Tetrahydrocarvylamine, *Carvomenthylamine*,

$$CH_3.CH<\begin{smallmatrix}CH(NH_2)-CH_2\\CH_2-CH_2\end{smallmatrix}>CH.CH(CH_3)_2,$$ boils at 212° (A. 277, 137).

Tert. Menthylamine, $CH_3.CH<\begin{smallmatrix}CH_2-CH_2\\CH_2-CH_2\end{smallmatrix}>C(NH_2)CH(CH_3)_2$, and **Tert. Carvomenthylamine**, $CH_3(NH_2)C<\begin{smallmatrix}CH_2-CH_2\\CH_2-CH_2\end{smallmatrix}>CH.CH(CH_3)_2$, have been obtained by the interaction of menthene hydrobromide, carvomenthene hydrobromide, and silver cyanate, with subsequent saponification (B. 26, 2270, 2562).

Menthene bases have been prepared by the reduction of the oximes of menthene ketones.

Dihydrocarvylamine, $C_{10}H_{17}NH_2$, boiling at 219°, with sp. gr. 0.889 (20°), $n_D = 1.48294$, is optically active, and is obtained from carvonoxime, $C_{10}H_{14}:NOH$. Its hydrochloride breaks down completely at 200° into ammonium chloride and terpinene, which in so doing passes partly into cymene (A. 275, 120; B. 24, 3984). **Carylamine**, $C_{10}H_{17}NH_2$, from caronoxime, is stable in the presence of potassium permanganate, but is rearranged by hydrochloric acid into isomeric *vestrylamine*, the hydrochloride of which yields carvestrene upon the application of heat. **Dihydroeucarvylamine**, $C_{10}H_{17}.NH_2$, is formed from eucarvoxime (B. 27, 3487). **α-Thujonamine**, $C_{10}H_{17}NH_2$, is obtained from the thujone oxime melting at 52°. Its hydrochloride, when heated, yields *thujene* or *tanacetene* (p. 312). The thujonoxime, melting at 90°, yields an *isomeric* **β-thujonamine**. A third **isothujonamine** results from isothujonoxime (A. 286, 96), melting at 119°. **Pulegonamine** (A. 262, 13; B. 29, R. 173).

Nitrolamines have been obtained from nitroso chlorides—*e.g.*, limonene—by transposition with primary and secondary bases.

4. THE RING-KETONES OF THE TERPAN OR MENTHAN GROUP.

Ketones like these are found in the vegetable kingdom. They are produced by the oxidation of the corresponding secondary alcohols, and by continued oxidation they change to cyclic and aliphatic carboxylic acids,—decomposition products,—the constitution of which furnish insight into the constitution of the ring-ketones and their derivatives. The ring-ketones of the terpan-group, like other ketones, are characterized by their oximes and the sparing solubility of their semicarbazones.

(*a*) **Ketomenthans, Ketohexahydro-p-cymene,** $C_{10}H_{18}O$.

Menthone, $CH_3 . CH<{CH_2 . CO \atop CH_2 . CH_2}>CH . CH(CH_3)_2$, boiling at 206°, sustains the same relation to menthol that camphor bears to borneol (p. 324). It occurs in American and Russian peppermint oils, together with menthol, esters of menthol, menthene, and limonene. Menthone is known in two optically active modifications. l-Menthone is obtained upon oxidizing menthol with potassium bichromate and sulphuric acid at a temperature not exceeding 50° (A. **250**, 322). Its sp. gravity equals 0.896 (20°), $[\alpha]_D = -28°$. Concentrated sulphuric acid, in the cold, rearranges l-menthone to d-menthone, $[\alpha]_D = +28°$.

The constitution of menthone (see p. 313) is demonstrated (1) by its conversion into 3-chlorcymene; PCl_5 changes menthone to *dichlorhexahydrocymene*, which splits off hydrogen chloride and becomes *tetrahydrochlorcymene*; this in turn, by the action of bromine and quinoline, loses hydrogen and 3-*chlorcymene* results (B. **29**, 314). (2) By the formation of *thymol* (p. 144) through the elimination of 2HBr from **Dibrom-menthone,** $C_{10}H_{16}Br_2O$, melting at 80°, which is produced in the bromination of menthone in chloroform solution (B. **29**, 418).

When l-menthone is reduced by sodium it forms l-*menthol*, while with ammonium formate the product is L-menthylamine (p. 317). Potassium permanganate oxidizes it to *oxomenthylic acid*, $CH_3 . CH<{CH_2 . CO_2H \atop CH_2 . CH_2 .}>CO . CH(CH_3)_2$, and *β-methyl adipic acid* (1, 454; B. **27**, 1820). Amylnitrite and hydrochloric acid convert menthone into nitrosomenthone and *menthoximic acid*, melting at 98°. This is the oxime of oxomenthylic acid (B. **29**, 27). Sodium and amyl formate change menthone to **oxymethylene menthone,** boiling at 121° (12 mm.). See B. **29**, 1599, for the condensation of menthone with aldehydes.

l-**Menthoxime** melts at 59° and boils at 250°; $[\alpha]_D = -42°$. When it is treated with PCl_5 in chloroform, or with acetic anhydride, or concentrated sulphuric acid, it becomes **iso-l-menthoxime,** melting at 119° and boiling at 295°; $[\alpha]_D = -52.25°$. P_2O_5 converts both oximes into **menthonitrile,** $C_9H_{17}CN$, boiling at 225°, which boiling sodium alcoholate changes to **menthoamide,** $C_9H_{17}CO . NH_2$, melting at 105°, and liquid **menthoic acid,** $C_9H_{17} . CO_2H$.

Tetrahydrocarvone, $CH_3 . CH . <{CO . CH_2 \atop CH_2 . CH_2}>CH . CH(CH_3)_2$ (constitution, see *carvomenthene*, p. 313), with sp. gr. 0.904 (20°), $n_D = 1.45539$, is produced in the oxidation of tetrahydrocarveol (p. 314). The *oxime* melts at 104°, the *α-isoxime* at 51°. *β-Isoxime* melts at 104°. The *semicarbazone* melts at 174° (A. **277**, 133; **286**, 107; B. **26**, 822). When oxidized with potassium permanganate or treated with amyl nitrite and hydrochloric acid, tetrahydrocarvone is decomposed like menthone with the production of an acid, $CH_3 . CO<{HOOC-CH_2 \atop CH_2-CH_2}>CH . C_3H_7$, *β-isopropyl-δ-acetyl valeric acid*.

isomeric with oxomenthylic acid. Energetic oxidation produces isopropyl succinic acid (B 29, 27).

Thujamenthone, boiling at 208°, with sp. gr. 0.891, $n_D = 1.44708$ (20°), results from the oxidation of thujamenthol (B. 28, 1959).

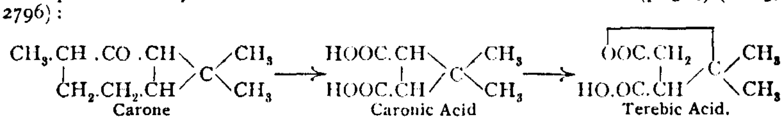
(*b*) **Ketomenthenes**, $C_{10}H_{16}O$, occur to a certain extent in nature, others are produced by the oxidation of the corresponding alcohols. They contain *one double* union.

d- and l-**Dihydrocarvone**, $\begin{matrix}CH_2\\CH_3\end{matrix}\!\!>\!C.CH\!<\!\begin{matrix}CH_2-CO\\CH_2-CH_2\end{matrix}\!>\!CH.CH_3$, boiling at 221°, with sp. gr. 0.928 (19°), $n_D = 1.47174$, are obtained from the corresponding dihydrocarveols. The *oximes* melt at 88°, and unite to the inactive [d + l]-*oxime*, melting at 115°. Boiling ferric chloride converts dihydrocarvone into carvacrol—compare carvenone and carone. Oxidation with potassium permanganate and afterward with chromic acid changes it to 2,5-*methyl acetyl cyclohexanone* (p. 316 and B. 28, 2147, 2704).

Carvenone, *Carveol*, boiling at 232°, with sp. gr. 0.927, $n_D = 1.4822$, is produced together with cymene when dioxyterpineol, melting at 121°, is digested with dilute sulphuric acid; also from dihydrocarvone with sulphuric acid (A. 286, 129). Its *oxime* melts at 91°, the *semicarbazone* at 202°. It resembles isothujone very much (B. 28, 1955).

Dihydroeucarvone, boiling at 87° (14 mm.), is obtained from dihydroeucarveol (p. 316) (B. 28, 646). The following ketones, carone and thujone, isomeric with the ketomenthenes, show the behavior of saturated ketones; hence it is assumed that double rings are present in them as in camphene and pinene.

Carone boils at 210°, being at the same time rearranged into carvenone. It results on treating dihydrocarvone hydrobromide with alcoholic potash. It reverts to dihydrocarvone hydrobromide again through the action of hydrobromic acid; whereas sulphuric acid changes it to oxytetrahydrocarvone. Carone is relatively stable toward potassium permanganate, which first attacks it at the water-bath temperature, forming **caronic acid**, $C_7H_{10}O_4$, cis melting at 175° (the *anhydride* melting at 55°), and trans- melting at 212°. We thus have a cis- and trans- modification of the acid, which would prove caronic acid to be an analogue of the trimethylenedicarboxylic acids. It is very probably dimethyl trimethylene-1,2 dicarboxylic acid; then in carone there would be a combined tri- and hexamethylene ring. Caronic acid is very stable; hydrobromic acid alone decomposes it readily and converts it into the isomeric **terebic acid** (p. 324) (B. 29, 2796):



Carone — Caronic Acid — Terebic Acid.

Thujone, *Tanacetone*, $\begin{matrix}(CH_3)_2.CH.CH.CH.CO\\ \qquad\quad CH_2.CH-CH.CH_3\end{matrix}$ (?) (compare the camphor formulas, p. 328), boiling at 200°, with sp. gr. 0.917 and $n_D = 1.4511$, occurs in the oil from *Tanacetum vulgare*, in that of worm-wood, in thuja-oil, oil of absinthe, and in that of *Artemisia Barellieri*. Potassium permanganate oxidizes thujone to *α*- and *β*-*thujaketone carboxylic acids*, melting at 74° and 78°. Upon the application of heat the *α*-acid is changed to the *β*-form, which probably has the constitution $CH_3.CO.CH_2.CH_2C[CH(CH_3)_2]:CH.COOH$, because upon oxidation it first passes into a *diketone*, $CH_3.CO.CH_2.CH_2.CO.CH(CH_3)_2$, and then into *ω-dimethyl lævulinic acid;* compare upon this point, as well as in regard to the constitution of thujone, isothujone and carvotanacetone (B. 30, 423, 429; 29, 885). Alcoholic sulphuric acid converts thujone into isothujone. When heated to 280° it is converted into carvotanacetone (B. 28, 1959). Its *oxime*, melting at 54°, is changed to carvacrylamine (B. 30, 325) by alcoholic sulphuric acid.

Isothujone boils at 231°; sp. gr. 0.927, with $n_D = 1.4822$. Formation—see thujone. Its *oxime* melts at 119°. The *α*- and *β*-*semicarbazones* melt at 208° and 148° (B. 28, 1955).

Carvotanacetone boils at 228°; sp. gr. 0.932 (21°), with $n_D = 1.47926$. Formation—see thujone. Its *oxime* melts at 119°. The *semicarbazone* melts at 177° (B. 28, 1959).

Pulegone, $CH_3 . CH<\begin{smallmatrix} CH_2 . CO \\ CH_2 . CH_2 \end{smallmatrix}>C = C(CH_3)_2$, boils at 221°; sp. gr. 0.936, with $n_D = 1.4846$. It is present in the ethereal oils from *Mentha pulegium* and *Hedeoma pulegoïdes*, which occur in commerce under the name *polei-oils*. The addition of hydrogen to pulegone produces menthene. *β-Methyl adipic acid* and acetone are produced by its oxidation, while it splits, upon heating with anhydrous formic acid, into acetone and 3-methyl hexanone, which is also oxidized to β-methyl adipic acid (A. 289, 337):

$$CH_3.CH<\begin{smallmatrix} CH_2.CO \\ CH_2.CH_2 \end{smallmatrix}>C = C(CH_3)_2 \xrightarrow{2H} CH_3.CH<\begin{smallmatrix} CH_2.CO \\ CH_2.CH_2 \end{smallmatrix}>CH.CH(CH_3)_2$$

$$\downarrow$$

$$CH_3.CH<\begin{smallmatrix} CH_2.CO \\ CH_2.CH_2 \end{smallmatrix}>CH_2(+ CO(CH_3)_2) \longrightarrow CH_3.CH<\begin{smallmatrix} CH_2.COOH \\ CH_2.CH_2 \end{smallmatrix}COOH.$$

When citronellal is condensed with acetic anhydride it yields a secondary cyclic alcohol—isopulegone—which is very similar to pulegone, and by hydrolytic decomposition yields 3-methyl-cyclohexanone (B. 30, 22). Isopulegone is reconverted into pulegone by long shaking with a baryta solution.

(*c*) **Menthadiën Ketones,** *Ketodihydro*-p-*cymenes*, $C_{10}H_{14}O$.—The most important member of this group is *carvone*, formerly called *carvol*. Its importance is due to its intimate relationship to carvacrol and limonene, which are isomeric with it. Carvone is known in three modifications, the d-, l-, and [d + l]-.

d-Carvone, $CH_3 . C\begin{smallmatrix} \diagup CO . CH_2 \diagdown \\ \diagdown CH \;.\; CH \diagup \end{smallmatrix}C . CH(CH_3)_2$ (B. 28, 31), or

$$CH_3 . \overset{*}{C}H\begin{smallmatrix} \diagup CO . CH \diagdown \\ \diagdown CH = CH \diagup \end{smallmatrix}C . CH(CH_3)_2, \text{ or } CH_3 . C\begin{smallmatrix} \diagup CH . CH_2 \diagdown \\ \diagdown CO \;.\; CH_2 \diagup \end{smallmatrix}\overset{*}{C}H . C\begin{smallmatrix} \diagup CH_3 \\ \diagdown CH_2 \end{smallmatrix} \; (?)$$

(B. 28, 2145), $[\alpha]_D = +62°$, boiling at 225°, occurs in oil of cumin and in dill-oil. When heated with potassium hydroxide or phosphoric acid it changes to isomeric carvacrol or 2-methyl-5-isopropyl-oxybenzene; hence it is assumed that in carvone the CO-group, like the OH-group in carvacrol, is in the ortho-position with reference to the methyl group. Reduction changes it to dihydrocarveol (p. 316), while ammonium formate converts it into dihydrocarvylamine (p. 317). Potassium permanganate oxidizes carvone to *oxyterpenylic acid*, $C_8H_{12}O_5$, which easily changes to a dilactone, $C_8H_{10}O_4$, melting at 129° (B. 27, 3333; 28, 2148). The carvones combine with hydrogen sulphide, hydrogen chloride, hydrogen bromide, and bromine (B. 28, R. 548).

l-**Carvone,** $[\alpha]_D = -62°$, boiling at 225°, occurs in curomoji oil (B 24, 81). It is obtained pure by distilling its hydrogen sulphide compound, melting at 187°, with caustic potash.

[d + l]-**Carvone,** boiling at 225°, is formed on mixing d- and l-carvone, as well as by oxidizing carveol methyl ether (p. 317). Formation from terpineol, B. 29, R. 587.

The three carvones are linked through the three carvoximes to the three corresponding limonenes. The carvoximes are prepared not only by the action of hydroxylamine upon the carvones, but also upon boiling the limonene nitrosochlorides with alcoholic potash. d-Carvone and l-limonene correspond on the one side to each other, while on the other l-carvone and d-limonene correspond, inasmuch as l-limonene nitrosochloride yields d-carvoxime, and d-limonene nitrosochloride l-carvoxime.

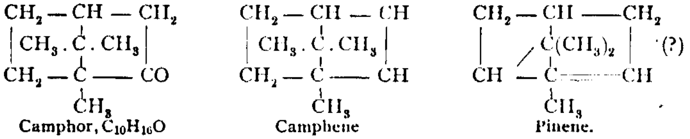
d-Carvoxime, $[\alpha]_D = +39.71°$, and **l-Carvoxime,** $[\alpha]_D = -39.34°$, melt at 72°. **[d + l]-Carvoxime** melts at 33° and is obtained from dipentene nitrosochloride (p. 312). Concentrated sulphuric acid rearranges carvoxime to p-amidothymol (compare p. 70, rearrangement of β-phenylhydroxylamine to p-amidophenol, A. 279, 366).

Eucarvone, $C_{10}H_{14}O$, boiling at 104° (25 mm.), with sp. gr. 0.948 (20°), results on treating carvone hydrobromide with alcoholic potash, and with methyl alcoholic potash at a definite temperature forms a deep-blue, unstable color. The *oxime* melts at 106°. The *semicarbazone*, $C_{10}H_{14}:N.NH.CO.NH_2$, melts at 184°. The reduction of eucarvone produces dihydroeucarveol (p. 316); see B. 29, 18, for its oxidation.

Isocarvone, $C_{10}H_{14}O$, boiling at 222–224°, with sp. gr. 0.989 (19°), $n_D = 1.5067$, results from the oxidation of isocarveol (p. 317). Its *oxime* melts at 98°.

C. CAMPHAN GROUP.

Camphor is the most important derivative of this group. Bredt considers it to be the ketone of a hexahydrobenzene in which two carbon atoms, occupying the p-position, are linked to each other by the group $CH_3.\overset{|}{\underset{|}{C}}.CH_3$. To one of these carbon atoms there is also attached a methyl group. It would, therefore, be necessary to assume that in the hydrocarbons closely allied to camphor there was probably a similar carbon skeleton present:



Camphor, $C_{10}H_{16}O$ Camphene Pinene.

Fenchone is very much like camphor. Hence, fenchene, derived from fenchone, will be classed with camphene and pinene.

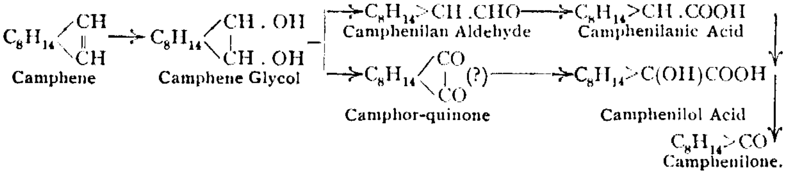
1. HYDROCARBONS.

Camphene, $C_{10}H_{16}$ (Constitution, see above), melting at 48° (53°) and boiling at 160°, $n_D = 1.45514$ (54°), is the only known *solid* terpene. It is known in a d-, l-, and an optically inactive modification; these are similar in chemical deportment. Camphene has been found, by a rearrangement, in isoborneol, in the oil from *Andropogon nardus*, and in camphor oil (B. 27, R. 163). It is obtained (1) from borneol by the action of potassium bisulphate at 200°; (2) by the action of $ZnCl_2$ or dilute sulphuric acid upon isoborneol; (3) when sodium acetate and glacial acetic acid at 200° act upon pinene hydrochloride; and (4) on digesting bornyl chloride (p. 325) with aniline.

Camphene Hydrochloride, $C_{10}H_{17}Cl$, melting at 149–151°, is produced when HCl is conducted into an alcoholic camphene solution. It is identical with the isobornyl chloride obtained from isoborneol (p. 325).

Camphene Dibromide, $C_{10}H_{16}Br_2$, melting at 89°, together with liquid **bromcamphene,** $C_{10}H_{15}Br$ (B. 29, 544, 697, 900), is formed when bromine in petroleum ether acts upon camphene. Camphene, treated with glacial acetic acid and concentrated sulphuric acid, yields *isoborneol acetate.*

Chromyl chloride in carbon bisulphide solution changes camphene to the compound $C_{10}H_{16} . 2CrO_2Cl_2$. Water decomposes this body, with the formation of an aldehyde—*camphenilan aldehyde*, $C_{10}H_{16}O$, melting at 70° and boiling at 96° (14 mm.). The oxidation of this aldehyde gives rise to two isomeric *camphenilanic acids*, $C_{10}H_{16}O_2$, melting at 65° and 118°, which can be changed through the corresponding *a-brom-acid* into *oxycamphenilanic acid*, camphenilol acid, $C_{10}H_{16}O_3$, melting at 171°. This latter acid is also formed when camphene is oxidized with potassium permanganate. Its further oxidation causes the elimination of carbon dioxide and the formation of a ketone, **Camphenilon**, $C_{10}H_{14}O$, melting at 35° and boiling at 81° (12 mm.). This is the lower ring-homologue of camphor (p. 326); it resembles the latter in odor and in chemical behavior. The camphenilan aldehyde and camphenilol-acid very probably owe their production to a camphene glycol (p. 325) and camphorquinone, formed at the first, but which sustain rearrangements like those of pinacone and benzilic acid. This change is represented in the following formulas (privately communicated by J. Bredt and Jagelki; compare C., 1897; I, 1056):



Dilute nitric acid converts camphene into tribasic **Carboxyl-apocamphoric Acid**, *Campho-acid*, $C_7H_{11}(CO_2H)_3$, melting at 196°; when heated this becomes dibasic apocamphoric acid (p. 322). Chromic acid oxidizes camphene to camphor.

Dihydrocamphene, $C_{10}H_{18}$, melting at 155° and boiling at 159°, is formed when sodium and alcohol act upon l-pinene hydrochloride and d-bornyl chloride. It is optically inactive, and sublimes with ease (v. Rosenberg, private communication).

Pinene, $C_{10}H_{16}$ (see above for constitution), boiling at 155°, with sp. gr. 0.858 (20°), $n_D = 1.46553$ (21°), is the chief ingredient of the turpentine oils obtained from the different varieties of pine. It also occurs in many other ethereal oils—eucalyptus, juniper-berry, sage, etc.

Turpentine Oil.—Turpentine, the resinous juice exuding from various Coniferæ, consists of a solution of resins in turpentine oil which distils with steam, while the resin (colophony) remains behind. Turpentine oil is a colorless liquid, boiling at 158–160°, with sp. gr. equaling 0.856–0.87. Its peculiar odor is due to the aldehyde-like oxidation products (B. 29, R. 871) produced by the action of sunlight.

It is almost insoluble in water, but is miscible with absolute alcohol and ether. It dissolves sulphur, phosphorus, and caoutchouc, and serves for the preparation of varnishes and oil-colors.

The turpentine oils, according to their origin, are distinguished by different rotatory power.

When turpentine is conducted through tubes heated to redness, isoprene (p. 309), toluene, m-xylene, naphthalene, anthracene, methyl anthracene, phenanthrene, etc., are produced. Heated with iodine, turpentine oil yields m-xylene, little p-xylene and cymene, pseudocumene, mesitylene, durene, and polyterpenes.

d-Pinene is obtained by the fractional distillation of American oil of turpentine, and **l-Pinene** from French oil of turpentine. They are, however, not chemically pure. If pinene nitrosochloride, easily obtained pure, be prepared from these modifications, and be then transposed with aniline, chemically pure *inactive pinene* will be obtained. Its properties will be similar to those above indicated.

Pinene contains *one* double linkage. It unites with 2Cl or 2Br, forming compounds, which change on heating to p-cymene and halogen hydrides.

The *dibromide* crystallizes and melts at 170°. Zinc-dust converts it into a terpene, melting at 65°, and isomeric with pinene and camphene; it apparently does not contain a double linkage (C. 1897, I, 1055). Pinene can be changed to camphene by means of concentrated sulphuric acid, or through its haloid acid addition products. It becomes dipentene when heated to 250–270°. Moist haloid acids convert pinene into dipentene dihydrohaloids (p. 311). Terpine hydrate is probably an intermediate product; it is formed when dilute nitric acid or sulphuric acid acts upon pinene.

d-Pinene Hydrochloride, *Artificial Camphor*, $C_{10}H_{17}Cl$, melting at 125° and boiling at 208°, is formed on conducting dry hydrochloric acid gas into well-cooled pinene. It is a white crystalline mass, with an odor like that of camphor. The hydrochloride from d-pinene is optically inactive, while the l-pinene hydrochloride is lævo-rotatory $[\alpha]_D = -30°$. **Pinene Hydrobromide** melts at 40° (A. **227**, 282). Camphene results from the splitting-off of hydrogen chloride or bromide.

Pinene Nitrosochloride, melting at 103°, is obtained by means of nitrosyl chloride, or amyl nitrite, glacial acetic acid, and hydrochloric acid. Hydrogen chloride in ether, when allowed to stand in contact with it, produces, just like limonene nitrosochloride (p. 311), hydrochlorcarvoxime (B. **29**, 12). **Pinene Nitrosobromide** melts at 92°. The bases readily change the pinene nitrosobromides into inactive nitrolamines. Sodium and alcohol reduce pinene nitrosochloride to **Nitrosopinene**, $C_{10}H_{14}:N.OH$, melting at 132° (B. **28**, 646), which yields pinylamine, $C_{10}H_{15}.NH_2$, by the action of zinc-dust and acetic acid.

The oxidation products of pinene have been studied quite thoroughly. Turpentine exposed to the air absorbs oxygen gradually, with the production of ozone. It resinifies at the same time with the formation of formic acid, acetic acid, and cymene in slight amount. See p. 325 for the production of pinol hydrate with the assistance of sunlight. Energetic oxidants, like nitric acid, produce *terebic acid* (p. 324), p-toluic acid, terephthalic acid, etc. *Terpenylic acid* is the chief product when the chromic acid mixture is the oxidant.

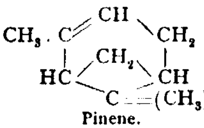
When pinene is carefully oxidized with potassium permanganate, pinene glycol is the immediate result, but the chief product resulting therefrom is **Pinonic Acid**, $C_{10}H_{16}O_3$, melting at 104° and boiling at 187° (15 mm.). It is a ketone-carboxylic acid. Other products are **pinoyl formic acid**, $C_{10}H_{14}O_4$, melting at 79°, a ketone dicarboxylic acid, and **nopic acid**, $C_{10}H_{16}O_3$, melting at 127°, which sulphuric acid converts into dihydrocuminic acid (B. **29**, 1923).

Pinonic acid is readily attacked. Bromine and alkali, or dilute nitric acid, oxidize it to the very stable **pinic acid**, $C_9H_{14}O_4$, melting at 102°. The latter acid, by means of the α-brom- and α-oxypinic acids, and oxidation of the last, give rise to **norpinic acid**, $C_{18}H_{12}O_4$, melting at 174°. The last two very stable acids very probably contain a tetramethylene ring corresponding to the formulas:

$$COOH.CH{<}{}^{CH_2}_{C(CH_3)_2}{>}CHCH_2CO_2H \qquad COOH.CH{<}{}^{CH_2}_{C(CH_3)_2}{>}CHCOOH$$

Pinic Acid — Norpinic Acid.

Baeyer, therefore, concurring with Wagner, assumes that in pinonic acid and pinene there is present a four-membered ring—a so-called *picean ring* (B. **29**, 2776):



(see p. 321).

Pinene.

The breaking-down of pinonic acid and pinoyl formic acid has also been attained in two other ways:

(1) Chromic acid changes pinonic acid to **ketoisocamphoric acid**, $C_{10}H_{17}O_5$, which is produced by the oxidation of campholenic acid (p. 328). Keto-isocamphoric acid can be broken down into **isocamphoronic acid**, $C_9H_{15}O_6$, and further into **dimethyltricarballylic acid**, $COOH.C(CH_3)_2CH(COOH)CH_2COOH$. The constitution of the latter has been proved by the decomposition of the corresponding oxy-acid into dimethyl succinic acid and oxalic acid when it is fused with caustic potash (compare oxycamphoronic acid, p. 333). The constitutional formulas of ketoisocamphoric acid, isocamphoronic

acid, and, therefore, that of pinonic acid, are at present subjects of controversy (see B. **29**, 2779, 3027).

(2) When pinonic acid is heated with acids there occurs an intermediate hydrolytic decomposition, followed by a rearrangement into **Homoterpenylic Methyl Ketone,**

[*Methoethylheptanonolide*], $\begin{array}{l}(CH_3)_2C\,.\,CH\,.\,CH_2\,.\,COO\\ \quad\;\; CH_2\,.\,CH_2\,.\,CO\,.\,CH_3\end{array}$, a substance which we have already learned was a decomposition product of terpinol (p. 316). Pinoylformic acid is similarly rearranged to **Homoterpenoylformic Acid,** $\begin{array}{l}(CH_3)_2C\,.CH\,.\,CH_2\,.\,COO\\ \quad\;\; CH_2\,.CH_2\,.CO.COOH.\end{array}$

These rearrangement products upon further oxidation yield (B. **29**, 2775):

Homoterpenylic Acid, $\begin{array}{l}(CH_3)_2C\,.\,CH\;\,.\,CH_2\,.\,COO\\ \quad\;\; CH_2\,.\,CH_2\,.\,COOH\end{array}$

Terpenylic Acid, . . . $\begin{array}{l}(CH_3)_2C\,.\,CH\;\,.\,CH_2\,.\,COO\\ \quad\;\; CH_2\,.\,COOH\end{array}$

Terebic Acid, . . . $\begin{array}{l}(CH_3)_2C\,.\,CH\,.\,CH_2\,.\,COO\\ \quad\;\; COOH\end{array}$

Terebic Acid, $C_7H_{10}O_4$, melting at 175°, was first obtained by oxidizing turpentine oil with nitric acid; it is also produced in the oxidation of terpenylic acid with potassium permanganate (B. **29**, 933). It behaves analogously to the paraconic acids. When heated it loses carbon dioxide and becomes *pyroterebic acid*, $(CH_3)_2C:CHCH_2COOH$, together with **isocaprolactone** and **teraconic acid**, $(CH_3)_2C:C(COOH)CH_2.COOH$, from which it can be re-formed by digestion with mineral acids. Baryta water converts terebic acid into the crystallizing barium salt of diaterebic acid or oxyisopropyl-succinic acid. See p. 319 for the formation of terebic acid from caronic acid.

Terpenylic Acid, $C_8H_{12}O_4$, melts at 90° when anhydrous. It is obtained by oxidizing turpentine oil with a chromic acid mixture and homoterpenylic acid with nitric acid (B. **29**, 2789). Upon distillation it yields **Teracrylic Acid,** $(CH_3)_2C:CH(CH_3)\text{-}CH_2.COOH$. Terpenylic acid, by reduction, becomes *β-isopropylglutaric acid* (see B. **29**, 920, 2621). See p. 320 for *oxyterpenylic acid.*

Homoterpenylic Acid, $C_9H_{14}O_4$, melting at 102°, results when homoterpenylformic acid is oxidized with nitric acid or with lead oxide (B. **29**, 1916).

The oxidation of pinene to pinonic acid and the hydrolytic rearrangement of the latter to homoterpenylic methyl ketone is certainly to be regarded as the reverse of the processes which take place in the hydrolytic rearrangement of pinene into terpine hydrate, terpineol (p. 316), and the oxidizing decomposition of the latter into homoterpenylic methyl ketone (above).

Fenchene, $C_{10}H_{16}$, boiling at 158-160°, with sp. gr. 0.864, $n_D = 1.469$, is optically inactive, and is formed on digesting fenchyl alcohol with potassium sulphate, or fenchyl chloride with aniline (A. **284**, 333). Fenchene can take up two bromine atoms. It is only attacked by nitric acid when heat is applied.

Tetrahydrofenchene, $C_{10}H_{20}$, boiling at 160-165°, with sp. gr. 0.7945 (22°), $n_D = 1.4370$, is produced when fenchone and fenchyl alcohol are heated with hydriodic acid.

Dihydrofencholene, C_9H_{18}—see fencholenic acid, p. 334.

2. **Alcohols.**—A. *Monacid Alcohols:* **Borneo Camphor, Borneol,** *Camphol,* $C_{10}H_{17}OH$, melting at 203° and boiling at 212°, occurs in three modifications in nature. d-Borneol is found in *Dryobalanops camphora*, a tree growing in Borneo and Sumatra, also in rosamary oil. l-*Borneol* and *inactive borneol* are present in the so-called baldrianic camphor. Many wood-spines contain it in the form of a fatty acid ester, more especially the acetic ester.

Borneol is very similar to Japan camphor, but has an odor at the same time resembling that of pepper. It sublimes very readily. d- and l-Borneol are formed simultaneously from camphor by reduction with sodium and alcohol (A. **230**, 225). Nitric acid oxidizes them to camphor. When borneol is heated with potassium bisulphate it breaks down into water and camphene (p. 321).

The *methyl ether* boils at 194° and the *ethyl ether* at 204° (B. **24**, 3713). The *acetyl ester* melts at 29°. It consists of rhombic, hemihedral forms. It boils at 98° (10 mm.), $n_D = 1.46635$, $[a]_D = +38° 20'$.

Bornyl Chloride melts at 148°. It results on treating borneol with PCl_5. Camphene is formed when it splits off hydrochloric acid.

Isoborneol, $C_{10}H_{17}OH$, melting at 212°, is even more volatile than borneol. It is produced when its acetate is saponified with alcoholic potash.

Its *acetate*, boiling at 107° (13 mm.), results upon digesting camphene and glacial acetic acid with concentrated sulphuric acid at 50–60° (D. R. P., 67255) (B. **27**, R. 102).

Camphol Alcohol, $C_{10}H_{19}OH$, boiling at 203°, is produced when campholamine hydrochloride (p. 326) is acted upon with silver nitrite (B. **27**, R. 126).

Camphel Alcohol, $C_9H_{17}OH$, melting at 25° and boiling at 179°, results from the interaction of camphelamine hydrochloride (p. 326) and silver nitrite. It is a tertiary alcohol. It readily decomposes into water and the hydrocarbon, C_9H_{16} (B. **27**, R. 126).

Fenchyl Alcohol, $C_{10}H_{17}.OH$, melting at 45° and boiling at 201°, with sp. gr. 0.933, is produced in two modifications: by the reduction of d- and l-fenchone (p. 333). It has a penetrating and very disagreeable odor. d-Fenchyl alcohol, $[a]_D = +10° 36'$, is obtained from l-fenchone, and l-fenchyl alcohol, $[a]_D = -10° 35'$, from d-fenchone (A. **284**, 331). See also tetrahydrofenchol.

Fenchyl Chloride, $C_{10}H_{17}Cl$, boiling at 85° (14 mm.), is produced when phosphorus pentachloride acts upon fenchyl alcohol. See fenchene.

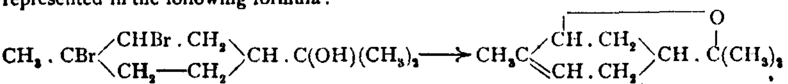
Isofencholen Alcohol, $C_{10}H_{17}OH$, boiling at 218°, with sp. gr. 0.927 (20°), $n_D = 1.476$, is produced when alcohol and sodium act upon fencholen amide (p. 333) (A. **284**, 337). It is readily attacked by potassium permanganate. When heated with dilute sulphuric acid it changes to **Fenchenol,** $C_{10}H_{18}O$, boiling at 183°, with sp. gr. 0.925 (20°), $n_D = 1.46108$. This compound, with the exception of the boiling point, can not be distinguished from cineol.

B. *Polyacid Alcohols:* **Camphene Glycol,** $C_{10}H_{16}(OH)_2$, melting at 192° and obtained from camphene by action of $KMnO_4$ (B. **23**, 2311), is converted by HCl into an oxide isomeric with camphor (probably camphenilan aldehyde, p. 322).

Pinene Glycol, $C_{10}H_{16}(OH)_2$, boiling at 145–147° (14 mm.), and obtained from pinene with $KMnO_4$ by the addition of hydroxyl groups to the unsaturated union, is converted by hydrochloric acid into pinol (B. **27**, 2270).

Pinol Hydrate, *Sobrerol,* $C_{10}H_{16}(OH)_2$, is known in three modifications. **d-Pinol Hydrate,** melting at 150°, $[a]_D = +150°$, and **l-Pinol Hydrate,** melting at 15?°, $[a]_D = -150°$, are produced when dextro- and lævo- turpentine oil are oxidized in the air on exposure to sunlight. [d + l]-Pinol hydrate results on treating pinol with hydrobromic acid and alkali, as well as upon mixing equimolecular quantities of d- and l-pinol hydrates. Pinol hydrate is an unsaturated compound. Bromine converts it into a *dibromide*, melting at 131°. Potassium permanganate changes it to a tetra-acid alcohol, **Sobreritrite,** $C_{10}H_{16}(OH)_4$, melting at 156° (B. **29**, 1195, R. 587).

Pinol, [d + l]-Sobrerone, $C_{10}H_{16}O$, boiling at 183°, with sp. gr. 0.953 (20°), $n_D = 1.46949$, is optically inactive. It is formed when the three pinol hydrates are treated with dilute sulphuric acid, and from the dibromide of terpineol (p. 316) by the splitting-off of 2HBr. It is as indifferent as cineol (p. 315) toward hydroxylamine, phenylhydrazine, and acid chlorides. This, as well as its formation from terpineol dibromide, is represented in the following formula:



Terpineol Dibromide Pinol.

Pinol hydrate is a hydrate corresponding to this oxide, an oxyterpineol, which results from pinene by the rupture of the picean ring (p. 323).

Pinol Dibromide, $C_{10}H_{16}Br_2O$, melting at 94° and boiling at 143° (11 mm.), is converted by sodium or alcoholic potash into pinol. Formic acid reduces it to cymene (A. **268**, 225). **Pinol nitrosochloride,** $C_{10}H_{16}O . NOCl$, melting at 103°, forms nitrolamines with bases. **Pinol Glycol,** $C_{10}H_{16}O(OH)_2$, melting at 125°, is obtained from pinol dibromide with silver oxide or lead hydroxide, or from its *diacetate*, melting at 97° (A. **268**, 223). An apparently isomeric glycol is produced in the oxidation of pinol with $KMnO_4$ (B. **28**, 2710).

Camphor Pinacone, $C_{20}H_{34}O_2$, melting at 176°, is formed, along with borneol, in the reduction of camphor (B. **27**, 2348; see also B. **29**, R. 675).

3. **Amines** have been obtained by the reduction of nitrosopinenes, oximes, and nitriles, as well as ketones with ammonium formate.

Bornylamine, $C_{10}H_{17} . NH_2$, melts at 159° and boils at 199°. The formyl compound is produced when camphor is heated with ammonium formate, and the base itself by the reduction of camphoroxime with alcohol and sodium. Bornylamine possesses an odor like that of camphor and piperidine. **Formyl-** and **Acetyl-bornylamine** melt at 61° and 141°. When heated to 200–210° with acetic anhydride they break down, with the production of camphene (A. **269**, 347). **Camphylamine,** $C_9H_{15} . CH_2 . NH_2$, boiling at 194–196°, is produced when the nitrile of campholenic acid is reduced. The *benzoyl compound* melts at 77° (B. **20**, 485; **21**, 1128).

Campholamine, $C_{10}H_{19} . NH_2$, and **Camphelamine,** $C_9H_{17}NH_2$,—see campholic acid (p. 328).

Fenchylamine and fencholenamine sustain the same relation to each other that we observed in bornylamine and camphylamine.

Fenchylamine, $C_{10}H_{17}NH_2$, boiling at 195°, with sp. gr. 0.9095 (22°), is known in three modifications, produced from the corresponding fenchones on heating them with ammonium carbonate, or by reducing the fenchone oximes. d-**Fenchylamine,** $[\alpha]_D = -24.89°$, is obtained from d-fenchone. The optical rotatory power of a series of derivatives has been studied:

Formyl-, Acetyl-, Propionyl-, Butyryl Fenchylamines, $[\alpha]_D = -36.56°$, $-46.62°$, $-53.16°$, 53.11° (A. **276**, 317).

Fencholenamine, $C_9H_{15} . CH_2 . NH_2$, boiling at 110–115° (21–24 mm.), results from the reduction of the nitrile of fencholenic acid (A. **263**, 138).

Pinylamine, $C_{10}H_{15} . NH_2$, boiling at 207° (760 mm.), 98° (20 mm.), with 0.943, is produced in the reduction of nitrosopinene (p. 323) (A. **268**, 197). Nitrous acid converts pinylamine into isocarveol (p. 317), a secondary alcohol.

Amidoterebenthene, $C_{10}H_{15} . NH_2$, boiling at 197–200° (760 mm.), is formed in the reduction of the decomposable nitroterebenthene, the product obtained when nitrous acid acts upon oil of turpentine. Its *hydrochloride*, $[\alpha]_D = -48.5°$, is lævo-rotatory, it being immaterial whether we proceed from the dextro- or lævo-rotatory turpentine oil (B. **22**, R. 108; **24**, R. 204).

4. **Ketones.**—Various transformation products of the ketones, $C_{10}H_{16}O$, *camphor* and *fenchone*, have been treated in the preceding sections. These ketones are similar in their chemical behavior, but are apparently different in constitution. By reduction they yield *borneol* and *fenchyl alcohol*, from which they are conversely again obtained by oxidation.

Phosphoric anhydride dehydrates them, and thus camphor yields p-*cymene*; and fenchone, m-*cymene*:

$$\text{Borneol} \xleftarrow{\;2H\;} \text{Camphor} \xrightarrow{-H_2O} \text{p-Cymene}$$

$$\text{Fenchyl Alcohol} \longleftarrow \text{Fenchone} \xrightarrow{-H_2O} \text{m-Cymene.}$$

Camphor is known in two optically active and one optically inactive modification, while fenchone is known in two optically active forms.

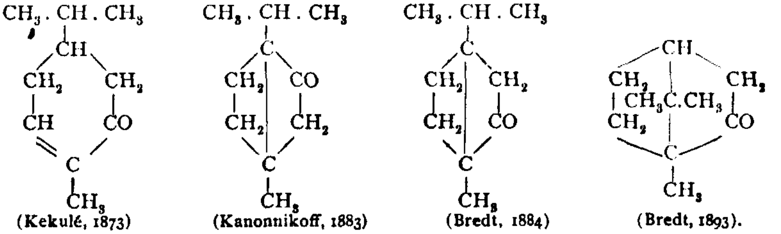
d-Camphor, Common Camphor, Japan Camphor, $C_{10}H_{16}O$, melting at 175° and boiling at 204°, with $[\alpha]_D = +44.22°$ in alcohol (A. **250**, 352), is found in the camphor tree (*Laurus camphora*). It is obtained by distillation with steam and sublimation. It is prepared artificially by oxidizing borneol with nitric acid and camphene with chromic acid. It is a colorless, transparent mass, crystallizes from alcohol, and sublimes in shining prisms of sp. gr. 0.985. It is very volatile, and is applied therapeutically. Its alcoholic solution is dextro-rotatory. Camphor yields pure cymene (p. 56) if distilled with P_2O_5, and on boiling with iodine forms carvacrol, $C_{10}H_{14}O$ (p. 145). When boiled with nitric acid it yields different acids, chiefly camphoric and camphoronic acids. Upon reduction it passes into borneol (p. 324).

l-Camphor, Matricaria Camphor, is contained in the oil of *Matricaria Parthenium*. It resembles d-camphor even to the rotatory power $[\alpha]_D = -44.22°$. It yields l-camphoric acid upon oxidation.

(d + l)-Camphor, melting at 178.6°, is produced on mixing d- and l-camphors, and by the oxidation of i-borneol and i-camphene with chromic acid (B. **12**, 1756).

Constitution of Camphor.—The camphor formula (1) proposed by Kekulé (1873) satisfactorily accounted for the change of camphor into p-cymene and carvacrol. However, the ready anhydride formation of camphoric acid, which had led to a seven-membered ring, could not be brought by it into accord with the known experiences relating to the anhydride formation of aliphatic dicarboxylic acids. The lack of additive power also remained unexplained. The formulas of Kanonnikoff and Bredt explained these relations far better. In them the p-carbon atoms of the hexagon of camphor were brought in direct union. The anhydride formation of camphoric acid, thus made parallel with ethylene succinic acid, could be understood on the basis of this formula. Baeyer (1893) showed that as camphoric anhydride melted *higher* than its hydrate, it probably contained an n-glutaric acid anhydride ring (A. **276**, 265).

Camphoric acid is not the only oxidation product of camphor, for when it is further oxidized camphanic acid and camphoronic acid are produced. In the latter acid J. Bredt recognized α,β-trimethyltricarballylic acid, inasmuch as it decomposed, upon the application of heat, into trimethyl succinic anhydride, isobutyric acid, carbonic acid, water and carbon; whereas when camphoronic acid. the lactone of oxycamphoronic acid, obtained from it, is fused with caustic potash, trimethyl succinic acid and oxalic acid are produced very readily. Bredt concludes from this deportment that the carbon grouping of camphoronic acid, as well as that of trimethyl succinic acid, must be present in camphanic acid, camphoric acid, and camphor. The formula of Bredt (1893) may be imagined (B. **26**, 3047) to have been evolved from that of Kekulé by rotating the isopropyl group about 180°, until it lies within the hexagon, and then its middle carbon atom is allowed to unite the two p-carbon atoms of the hexagon by the migration of an H atom and the dissolution of the double union:

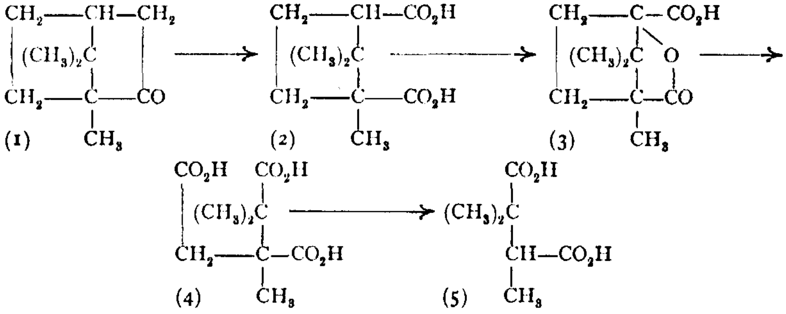


(Kekulé, 1873) (Kanonnikoff, 1883) (Bredt, 1884) (Bredt, 1893).

The position of the CO-group is proved by the conversion of camphor into carvacrol (above).

The oxidation of camphor (1) to camphoric acid (2), camphanic acid (3), and campho-

ronic acid (4), as well as the decomposition of the latter into trimethyl succinic acid (5), also found among the oxidation products of camphor (B. **26**, 2337), is represented in the following diagram :



The partial synthesis of camphor by the distillation of calcium homocamphorate harmonizes with this conception of the constitution of camphor (Ch. Z., 1895, **19**, 1755).

New formulas for borneol, camphene, and many other derivatives closely related to camphor, can be deduced from the camphor formula.

Transposition Products of Camphor.—Chlorine and bromine convert camphor into mono- and disubstitution products. *α*- and *β*,d-*Chlor-camphor* melt at 92° and 100°. *α*- and *β*-*Dichlor-camphor* melt at 93° and 77°, while *α*- and *β*-*Brom-camphor* melt at 76° and 61°. Consult C., 1897, I, 601, for the action of sodium upon brom-camphor: **Dicamphor**, $(C_{10}H_{15}O)_2$, etc.

PCl_5 converts camphor into **Camphor-dichloride** (A. **19**, 259), melting at 155°.

Two *Chlornitrocamphors* (*α* and *β*) are produced when chlorcamphor is digested with nitric acid; the copper and zinc couple reduces them to *α*- and *β*-*nitrocamphor* (B. **22**, R. 266; **23**, R. 115; **29**, R. 270).

See B. **28**, R. 643; **29**, R. 512, for the camphor-sulphonic acids and their transformation products.

Camphoroxime, $C_{10}H_{16}$: NOH, melts at 118° and boils at 249° (A. **259**, 331). Its odor resembles that of camphor. See B. **29**, R. 1107, for its preparation. Bornylamine is formed in its reduction (p. 326). *Camphorsemicarbazone*, $C_{10}H_{16}$: N . NH . CO . NH_2, melts at 237° (B. **28**, 2191).

Camphorimine, $C_{10}H_{16}$: NH,—see B. **29**, 2807; C., 1897, I, 814.

Campholic Acid, C_9H_{17} . CO_2H, melting at 95°, is formed when camphor is heated with sodium in xylene (B. **28**, R. 376), or from sodium-camphor at 288°. Boiling nitric acid oxidizes it to camphoric and camphoronic acids (B. **27**, R. 752). The *amide* melts at 79°. The *nitrile* melts at 72° and boils at 218°. It yields *campholamine*, $C_{10}H_{19}NH_2$, melting at 210°, upon reduction. Bromine and caustic alkali change the amide to *Camphelylisocyanate*, boiling at 201°, from which *Camphelamine*, $C_9N_{17}NH_2$, melting at 43° and boiling at 175°, is obtained (B. **26**, R. 21; **27**, R. 126). **Isocampholic Acid**, B. **29**, R. 356. The camphor-ring in camphoroxime can be very easily ruptured by mineral acids, the products being *α*- and *β*-campholene nitrile, isoaminocamphor, and dihydrocampholene lactone.

α-Campholenic Acid,

$$\begin{array}{l} CH_2 - CH - CH_2 \\ | \qquad\quad >C(CH_3)_2 \; | \\ CH = C - CH_3 \quad COOH \end{array}$$

, boils at 256°. Its sp. gr. equals 0.992 (19°). It is optically active, $n_D = 1.47125$. The *nitrile*, b. p. 226°, of this acid is produced with water exit when dilute sulphuric acid acts upon camphoroxime. The reduction of the nitrile produces *α*-*Camphylamine*, $C_{10}H_{17}NH_2$, boiling at 195°. Alcoholic potash saponifies it to *α*-*campholamide*, melting at 130°, and finally to the acid. The latter is oxidized by potassium permanganate to:

α-**Dioxyhydrocampholenic Acid**, $C_9H_{15}(OH)_2CO_2H$, melting at 144°, and a ketonic acid, **l-Pinonic Acid, which affords decomposition products similar to those of**

the like-named oxidation product of pinene (p. 324). Chromic acid oxidizes α-campholen- or dihydrodioxycampholenic acid to **Isoketocamphoric Acid**, $C_{10}H_{16}O_5 = CH_3$-$CO.C(CH_3)_2CH(CH_2COOH)_2$ (?), and eventually to **Isocamphoronic Acid**, CO_2HC-$(CH_3)_2CH(CH_2COOH)_2$ (?), m. p. 167°. Concentrated sulphuric acid, when warmed with the latter body, sets free CO_2, and terpenylic acid results (B. **29**, 3006).

β-**Campholenic Acid**, melting at 52° and boiling at 245°, is optically inactive. Its *nitrile*, boiling at 220–230°, is produced in the action of stronger acids (concentrated HI) upon camphoroxime. It is reduced to β-**camphylamine**, melting at 197°, which may be saponified to an *amide*, melting at 86°. Potassium permanganate oxidizes β-campholenic acid to a dihydroxy-acid, melting at 146°, and with it an oily acid which readily changes to *isocamphorone*, $C_9H_{14}O$, boiling at 217°. Chromic acid oxidizes the β-acid to γ-**acetylisocapronic acid**, $CH_3.CO.C(CH_3)_2CH_2CH_2COOH$, melting at 48°. Further oxidation leads to a decomposition into α-dimethylglutaric acid and α-dimethylsuccinic acid. The same decomposition products are obtained from isocamphorone (B. **30**, 242). The conversion of β-campholenic acid, when heated with bromine, into 1,3,4-xylyl-acetic acid (B. **29**, R. 643) is peculiar.

Dihydrocampholene Lactone, $\begin{array}{l}CH_2—CH———————CH_2\\ |\qquad\qquad\quad >C(CH_3)_2\ \ |\\ CH_2—C(CH_3)<—O—CO\end{array}$, melting at 30° and boiling at 256°, appears as the principal or the by-product in the decompositions of camphoroxime by strong acids, and may be obtained by acids from the two campholenic acids, as well as from isoaminocamphor. Chromic acid oxidizes it to oxydihydrocampholene lactone, melting at 144° (B. **30**, 404).

Isoamino-camphor, $C_{10}H_{17}ON$, boiling at 254° (760 mm.), 152° (65 mm.), is formed along with the preceding bodies when stronger acids act upon camphoroxime, campholenamides, and nitriles. It apparently contains a primary amine group, and is very similar to the isomeric amido-camphor (p. 330). It changes quite readily to dihydrocampholenolactone. Compare B. **30**, 324, for its constitution.

Campholene, $\begin{array}{l}CH—CH(CH_3)\\ \|\qquad\qquad\quad >C(CH_3)_2\\ CH—CH(CH_3)\end{array}$ or $\begin{array}{l}CH = C(CH_3)\\ |\qquad\qquad\quad >C(CH_3)_2\\ CH_2—CH(CH_3)\end{array}$ (?), boiling at 134°, is produced when α- or, better, β-campholenic acid has been heated. Carbon dioxide is eliminated. It is, further, formed when P_2O_5 acts upon the chloride of campholic acid. The *dibromide* melts at 97°. Campholene, heated with HI-acid to 280°, becomes hexahydropseudocumene, just as β-campholenic acid changes to xylyl-acetic acid (B. **30**, 594), and camphoric acid to tetrahydroisoxylene (B. **26**, 3053).

An apparently isomeric **Campholene**, C_9H_{16}, boiling at 137°, has been obtained together with carvacrol from chlor-camphor by the action of zinc chloride (B. **26**, R. 492).

Nitrous acid, or sodium bisulphite and boiling dilute sulphuric acid, act upon isonitrisocamphor, and the product is *camphor-quinone*, which is also formed in the oxidation of camphocarboxylic acid (B. **27**, 1447). **Camphor-quinone**, $C_8H_{14}<\begin{array}{l}CO\\ |\\ CO\end{array}$, resembles quinone and the α-diketones. Its odor is peculiarly sweet. It volatilizes with aqueous vapor and sublimes at 60° in golden yellow needles that melt at 198° (A. **274**, 71).

Zinc-dust and hydrochloric acid or aluminium amalgam reduce it to α-**Oxycamphor**, $C_8H_{14}<\begin{array}{l}CH.OH\\ |\\ CO\end{array}$, melting at 203–205°, which may be reoxidized to camphor-quinone. The latter, under the influence of various reagents, changes to derivatives of camphoric acid (compare B. **30**, 657, 659).

Isonitroso-camphor, $C_8H_{14}<\begin{array}{l}CO\\ |\\ C:N.OH\end{array}$, is obtained by the action of amyl nitrite and sodium ethylate upon camphor. The compound melts at 153°. Concentrated sulphuric acid converts it into the imide of camphoric acid (B. **26**, 241), while acetyl chloride, PCl_5 or soda and acetic anhydride change it to the mono-nitrile of camphoric acid (B. **29**, R. 651). Zinc and dilute acids reduce it to amido-camphor (A. **274**, 71).

Camphor-dioximes—α-dioxime, m. p. 181°; β-dioxime, m. p. 220°—result on treat-

ing isonitroso-camphor with hydroxylamine acetate. γ-*Dioxime*, m. p. 131°, is made by treating isonitroso-camphor with free hydroxylamine (B. **26**, 243). An isomeride of the camphor dioxime is—

Pernitroso-camphor, $C_{10}H_{16}N_2O_2$, melting at 43°, which results from the interaction of nitrous acid and camphoroxime, and changes, upon treatment with concentrated sulphuric acid, to **Isocamphor**, $C_{10}H_{16}O$ (B. **29**, R. 1106).

Amido-camphor, $C_8H_{14}\left\langle\begin{array}{l}CH\,.\,NH_2\\ |\\ CO\end{array}\right.$, boiling at 244°, is produced when isonitroso-camphor is reduced. It is a paraffin-like mass; it has a fishy odor. Its *hydrochloride*, melting at 224°, acts similarly to, although not so powerfully as, curare. Its *acetyl derivative* melts at 108° (A. **274**, 91).

Azocamphor, *Monoketazocamphor-quinone*, $C_8H_{14}\left\langle\begin{array}{l}C\left\langle\begin{array}{l}N\\ \|\\ N\end{array}\right.\\ |\\ CO\end{array}\right.$, melts at 74°. It forms yellow-colored crystals. It is produced when nitrous acid acts upon the hydrochloride of amido-camphor (B. **26**, 1718). Potassium sulphite changes it to a hydrazine-sulphonate, which concentrated hydrochloric acid decomposes into hydrazine and camphor-quinone (B. **29**, R. 1115).

Camphenone, $\begin{array}{l}CH_2\text{——}C\diagdown\\ |\qquad\quad\ \ |\ \ \diagdown CH\\ |\ (CH_3)_2C\ \ \ |\\ |\qquad\quad\ \ |\ \diagup CO\\ CH_2\text{——}C(CH_3)\end{array}$ (?), melting at 168–170°, is formed, together with azocamphenone, when azocamphor is heated. It has an odor like that of camphor. Its *oxime* melts at 132° (B. **27**, R. 590). Consult B. **29**, R. 1108, for the action of bromine and hydrogen bromide.

Azocamphenone, $C_8H_{14}\left\langle\begin{array}{l}CNN:C\\ |\qquad\ \ |\\ CO\quad OC\end{array}\right\rangle C_8H_{14}$, melts at 222° (B. **27**, R. 892).

Oxymethylene-camphor, $C_8H_{14}\left\langle\begin{array}{l}C=CH\,.\,OH\\ |\\ CO\end{array}\right.$, melting at 77°, is produced when sodium or sodium ethylate and formic ester act upon camphor (A. **281**, 306). Hydroxylamine changes oxymethylene camphor into the oxime of formylcamphor and cyancamphor.

Chlormethylene-camphor, $C_8H_{14}\left\langle\begin{array}{l}C=CHCl\\ |\\ CO\end{array}\right.$, boiling at 119° (16 mm.), is produced when PCl_3 acts upon oxymethylene-camphor.

Oxymethylene-camphor Anhydride, $[(C_8H_{14}CO)=CH]_2O$, melting at 188°, is obtained from the sodium salt of oxymethylene-camphor and chlormethylene-camphor.

The *methyl ether*, $(C_{10}H_{14}O)=CHOCH_3$, melting at 40° and boiling at 262°, is obtained (1) from oxymethylene-camphor, sodium ethylate, and methyl iodide, (2) from chlormethylene camphor and sodium methylate, and (3) from oxymethylene-camphor, methyl alcohol, and hydrochloric acid. The *acetate*, $(C_{10}H_{14}O)=CH\,.\,O\,.\,CO\,.\,CH_3$, melting at 63° and boiling at 290–293°, is obtained from oxymethylene-camphor and acetic anhydride.

Oxymethylene-camphor Cyanhydrin, $C_8H_{14}\left\langle\begin{array}{l}CH\,.\,CH(OH)CN\\ |\\ CO\end{array}\right.$, melting at 122°, is formed from oxymethylene-camphor, glacial acetic acid, and potassium cyanide. When boiled with acetic anhydride it yields—

Cyanmethylene-camphor, $C_8H_{14}\left\langle\begin{array}{l}C=CH\,.\,CN\\ |\\ CO\end{array}\right.$, melting at 46° and boiling at 280°. Hydrochloric acid converts it, when heated to 120° in glacial acetic acid solution, into

Camphor-methylene Carboxylic Acid, $C_8H_{14}\left\langle\begin{array}{l}C=CH\,.\,CO_2H\\ |\\ CO\end{array}\right.$, melting at 101°.

d-Camphor-carboxylic Acid, $C_8H_{14}\left\langle\begin{array}{l}CH\,.\,CO_2H\\ |\\ CO\end{array}\right.$, melts, with carbon dioxide evo-

lution, at 128°. It is obtained from sodium camphor and carbonic acid (B. **24**, 3382). Its esters yield sodium compounds, which, heated with alkylogens, produce *alkyl-camphocarboxylic esters*, whose acids, when heated, evolve carbon dioxide and break down into *alkyl-camphor*.

d-Cyan-camphor, $C_8H_{14}<\begin{matrix}CH.CN\\ |\\ CO\end{matrix}$, melting at 127°, is produced when cyanogen is conducted into sodium camphor, and by digesting a solution of sodium oxymethylene-camphor with hydroxylamine hydrochloride (A. **281**, 349). Alkalies and alkylogens convert it into *alkyl-cyan camphor*.

Camphoric Acid.—There are four optically active and two inactive camphoric acids.

d-Camphoric Acid, *ordinary camphoric acid* (Constitution, p. 328), $C_8H_{14}(CO_2H)_2$, m. p. 187°, $[\alpha]_D = +49.7°$ in alcohol, is obtained by heating d-camphor or campholic acid with nitric acid (A. **163**, 323), and because it can be made without great trouble, has been exhaustively studied. When it is heated above the melting point, or when treated with acetyl chloride (A. **226**, 1), it changes to its **anhydride**, melting at 221° and boiling at 270°. The acid is dextro-rotatory.

By fusion with caustic potash, camphoric acid changes to isopropyl succinic acid and l-isocamphoric acid; by oxidation with nitric acid, camphoronic acid and dinitrocapronic acid, $\begin{matrix}(CH_3)_2C.CO_2H\\ |\\ CH_3.C(NO_2)_2\end{matrix}$, are produced, while with chromic acid the products are camphoronic and trimethyl succinic acids. Water and bromine change it to camphanic acid (B. **28**, 2151). Compare B. **30**, 289, for the oxidation of camphoric acid with potassium permanganate. The distillation of calcium camphorate yields **Camphorphorone,** $\begin{matrix}CH_2—C=C(CH_3)_2\\ |\\ CH_2—CH(CH_3)_2.CO\end{matrix}$, boiling at 195–200°. It is oxidized by potassium permanganate to α-methylglutaric acid (B. **26**, 3053). Tetrahydro- and hexahydroisoxylene are produced when camphoric acid is heated with hydriodic acid.

The d-camphoric acid forms two series of acid esters: the *allo-esters*, produced by the partial saponification of the neutral esters, and the *ortho-esters*, resulting from the partial esterification of the acids (B. **26**, 289).

See B. **26**, 600, R. 87, 614, 688, for the electrolysis of the ester acids.

The *dichloride*, $C_8H_{14}<\begin{matrix}CCl_2\\ CO\end{matrix}>O$, boils at 140° (15 mm.) (B. **23**, R. 229).

The *diamide*, $C_8H_{14}C_2O_2(NH_2)_2$, melting at 197°, is converted by potassium hypobromite into $C_{10}H_{16}N_2O_2$, melting at 235°. This is probably the ureïde of an oxyacid (B. **27**, R. 894) corresponding to campholactone. Two isomeric **Camphor-amino-acids,** melting at 177° and 180°, have been obtained from the anhydride with ammonia, and from the imide with sodium hydroxide (B. **29**, R. 96).

The *imide*, $C_8H_{14}C_2O_2NH$, melting at 248° and boiling at 300°, is also formed from isonitrosocamphor (B. **26**, 58, 242; A. **257**, 308).

The *methyl imide*, $C_8H_{14}<\begin{matrix}CO\\ CO\end{matrix}>NCH_3$, melting at 40–42°, is obtained from silver camphoronimide and methyl iodide, as well as by heating *methyl isoimide* above its melting point (B. **29**, R. 96).

Methyl Isoimide, $C_8H_{14}<\begin{matrix}C=N.CH_3\\ CO>O\end{matrix}$, melting at 134°, results when camphor-methyl-amino-acid is treated with acetyl chloride or PCl_3 (B. **26**, R. 688).

Camphoryl Hydroxylamine, $C_8H_{14}<\begin{matrix}CO\\ CO\end{matrix}>N.OH$, melts at 225° (B. **27**, R. 893).

Camphor-nitrilo-acid, cyanlauronic acid, $C_8H_{14}(CN)COOH$, melting at 152°, is formed when camphor-amino-acid is treated with acetyl chloride and subsequently with ammonia,

or by the interaction of acetyl chloride and isonitrosocamphor (p. 329 and B. **29**, R. 651, 779).

l-**Camphoric Acid** results from the oxidation of matricaria camphor. It resembles the d-variety in every particular, even to the rotatory power.

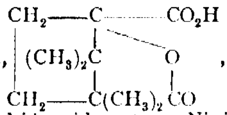
[d + l]-**Camphoric Acid**, *Paracamphoric Acid*, melting at 204°, is formed upon mixing alcoholic solutions of equimolecular quantities of d- and l-camphoric acids (B. **23**, R. 229).

d-**Isocamphoric Acid**, *d-cistrans-camphoric acid*, melting at 171°, with $[\alpha]_D = +48°$, may be prepared by heating l-camphoric acid with water, or, better, with a mixture of glacial acetic acid and hydrochloric acid. It does not form a real anhydride, hence can be easily separated by means of acetyl chloride from the l-camphoric acid.

l-**Isocamphoric Acid**, $[\alpha]_D = -48°$, is obtained from both d-camphoric acid and its chloride.

[d + l]-**Isocamphoric Acid**, melting at 191°, results from the union of d- and l-isocamphoric acids. When they are heated the corresponding camphoric anhydrides are produced (B. **27**, 2001). Compare B. **29**, 1700, for the crystal forms of the camphoric acids.

Brom-camphoric Anhydride (Constitution; see camphanic acid), $C_{10}H_{11}BrO_3$, melts at 215°.

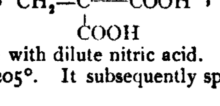
Camphanic Acid, , melting at 201°, is obtained on boiling brom-camphoric anhydride with water. Nitric acid oxidizes it to camphoronic acid. By distillation camphanic acid loses carbon dioxide, and becomes campholactone and lauronolic acid (A. **227**, 1). Compare B. **29**, R. 772, 861, for additional brom- and oxy-camphoric acids.

Lauronolic Acid, $C_8H_{13}.CO_2H$, is a colorless oil. It is formed when soda acts on brom-camphoric anhydride. Upon standing, or by boiling in hydrochloric acid solution, it rearranges itself to **Campholactone**, $C_8H_{14}\left\langle\begin{matrix}CO\\|\\O\end{matrix}\right.$, melting at 50° (A. **227**, 5).

Isolauronolic Acid, $C_8H_{13}.CO_2H$, melting at 134°, is obtained from sulphocamphylic acid heated to 200°, as well as by the action of Al_2Cl_6 upon camphoric anhydride (C., 1897, I, 763).

Sulphocamphylic Acid, *Sulphocamphoric Acid*, $C_9H_{16}SO_6 + 2H_2O$, melting at 160–165°, is produced in the action of sulphuric acid upon camphoric acid. Upon heating it changes to isolauronolic acid, and upon oxidation with nitric acid yields sulphoisopropyl-succinic acid and dimethylmalonic acid (B. **26**, 2044).

Campholide, $C_8H_{14}<\begin{matrix}CH_2\\CO\end{matrix}>O$, melting at 211°, is formed in the reduction of camphoric anhydride with alcohol and sodium amalgam, just as phthalide is obtained from phthalic anhydride (B. **29**, R. 221, 288). The lactam, $C_8H_{14}<\begin{matrix}CH_2\\CO\end{matrix}>NH$, melting at 229°, being analogous to the phthalimidines, may be designated *campholimidine*. It results upon heating the hydrochloride of the corresponding amido-acid, produced in the reduction of camphor-nitrilo-acid (B. **29**, 98, 652).

Carboxyl-apocamphoric Acid, *Campho-acid*, , melting at 196–200°, is produced in the oxidation of camphene with dilute nitric acid. It forms an *anhydride acid* when it is heated. This melts at 205°. It subsequently splits off CO_2 and passes into the anhydride of—

Apocamphoric Acid, *Camphopyro-acid*, , melting at 204°. It behaves analogously to camphoric acid (B. **29**, R. 175, 773; Ch. Zt., 1896, p. 840).

d-Homocamphoric Acid, *Hydroxycamphocarboxylic Acid*, $C_8H_{14}<^{CH_2.COOH}_{CO_2H}$, melting at 234°, is produced when cyan-camphor is boiled with aqueous caustic potash. Its *mononitrile* is formed on heating campholide (see this) with potassium cyanide (B. 29, R. 288). d-Camphor is obtained on heating calcium homocamphorate in a current of carbon dioxide.

d-Hydro-camphorylacetic Acid, $C_8H_{14}<^{CH_2.CH_2.CO_2H}_{CO_2H}$, melting at 142°, is produced when hydrocamphorylmalonic acid is heated (A. 257, 303).

d-Hydrocamphorylmalonic Acid, $C_8H_{14}<^{CH_2.CH(CO_2H)_2}_{CO_2H}$, melting at 178°, is obtained by the reduction of camphorylmalonic ester (A. 257, 301).

d-Camphorylmalonic Ester, $C_8H_{14}\begin{matrix} \diagup C=C(CO_2C_2H_5)_2 \\ >O \\ \diagdown CO \end{matrix}$, melting at 82° and boiling at 274° (40 mm.), results from the action of sodium malonic ester upon the chloride of camphoric acid.

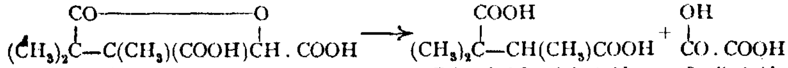
Camphoronic Acid, *α,β-Trimethyltricarballylic Acid*,

$\begin{matrix} (CH_3)_2C & — & C(CH_3) & — & CH_2 \\ | & & | & & | \\ COOH & & COOH & & COOH \end{matrix}$, is produced in the oxidation of camphoric acid, camphanic acid, and campholic acid with nitric acid.

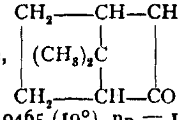
It has been synthesized in the following manner: acetoacetic ester and α-bromisobutyric ester are condensed by zinc to β-oxy-α,β-trimethylglutaric ester, $COOR.CH_2\text{-}C(OH)(CH_3)C.(CH_3)_2COOR$, which PCl_5 converts into the ester of the β-chlor-acid, and the latter is then changed by potassium cyanide to the ester of β-cyan-α,β-trimethylglutaric acid, the mononitrile of camphoronic acid, which is then saponified to camphoronic acid (C., 1897, 1, 813).

The importance of camphoronic acid in the determination of the constitution of camphor has been explained (p. 328). Camphoronic acid melts at 135°, changing at the same time into *camphoro-anhydridic acid*, melting at 135° and boiling at 205° (12 mm.). The *chloride* of the latter acid is converted by bromine into two isomeric *bromcamphoro-anhydridic acid chlorides*; one of these, when boiled with water, forms the lactone of unstab'e oxycamphoronic acid, *camphoranic acid*, while the other, under similar treatment, yields a stable *oxycamphoronic acid*, melting at 248°. Camphoronic acid, upon distillation, breaks down into trimethyl succinic anhydride, iso utyric acid, CO_2, H_2O, and carbon.

Camphoranic Acid, $C_9H_{12}O_4 + H_2O$, melting at 209°, is a lactonic acid which resists decomposition by alkalies very strongly. When fused with caustic potash it is readily split into trimethyl succinic acid and oxalic acid (privately communicated by J. Bredt):



Camphoranic Acid — Trimethyl Succinic Acid — Oxalic Acid.

Fenchone,  (?), melting at + 5° and boiling at 192–194°, with sp. gr. 0.9465 (19°), $n_D = 1.46306$, is known in two isomeric modifications. It is the ketone of all known ketone derivatives of the terpenes which is most like camphor in its behavior.

d-Fenchone, $[\alpha]_D = +71.70°$, was discovered in 1890 by Wallach and Hartmann, while **l-Fenchone**, $[\alpha]_D = -66.94°$, was found in 1892 by Wallach, together with pinene and thujone or tanacetone, in the oil of thuja. It is very stable toward concentrated nitric acid. Potassium permanganate oxidizes it to dimethylmalonic acid, acetic

acid, and oxalic acid. When reduced it passes into d- and l-fenchyl alcohol (p. 325) and tetrahydrofenchene (p. 324). With conditions analogous to those under which camphor yields p-cymene, fenchene will yield m-cymene—*e. g.*, upon heating with P_2O_5. Fenchone does not form an oxymethylene derivative.

Fenchonoxime, $C_{10}H_{16}$: NOH, melts at 161° and boils at 240°; $[\alpha]_D = + 65.94°$ (see B. **29**, 2818).

Fencholenic Acid, $C_9H_{15}.CO_2H$, boiling at 260°, with sp. gr. 1.0045, $n_D = 1.4766$, is obtained from its amide (*a-isofenchonoxime*) and its nitrile (fenchonoxime anhydride) by saponification with alcoholic potash. Hydriodic acid reduces it to *dihydrofencholene*, C_9H_{18}, boiling at 140°, with sp. gr. 0.79 (20°), $n_D = 1.43146$. The *amide* (*a-isofenchonoxime*), melting at 113°, results when the nitrile is acted upon with alcoholic potash. The *nitrile* (*fenchonoxime anhydride*), boiling at 217°, with sp. gr. 0.898 (20°), $n_D = 1.46108$, $[\alpha]_D = + 43.31°$, is produced on gently heating fenchonoxime with dilute sulphuric acid.

β-Isofenchonoxime, $C_{10}H_{17}NO$, melting at 137°, is formed when *a-isofenchonoxime* is boiled with dilute sulphuric acid. It is a monobasic body, probably a lactam (B. **28**, R. 456).

RESINS.

The resins are closely related to the terpenes, and occur with them in plants, and are also produced by their oxidation in the air. Their natural, thick solutions in the essential oils and turpentines are called *balsams*; whereas the true *gum resins* are amorphous, mostly vitreous bodies. Their solutions in alcohol, ether, or turpentine oils constitute the commercial *varnishes*.

Most natural resins appear to consist of a mixture of different, peculiar acids, the resin acids. The alkalies dissolve them, forming *resin soaps*, from which acids again precipitate the *resin acids*. By their fusion with alkalies we obtain different benzene derivatives (resorcinol, phloroglucin, protocatechuic acid); and when they are distilled with zinc-dust they yield benzenes, naphthalenes, etc.

Colophony is found in turpentine (p. 322) and, in the distillation of the latter, remains as a fused mass. It consists principally of **Abietic Acid,** $C_{19}H_{28}O_2$ (Sylvic acid), which can be extracted by hot alcohol, crystallizes in leaflets, and melts at 139° (147°). When oxidized it yields trimellitic, isophthalic, and terebic acids.

Gallipot Resin, from *Pinus maritima*, contains **pimaric acid,** $C_{20}H_{30}O_2$, which is very similar to sylvic acid and passes into the latter when distilled in vacuo. It melts at 210°. The latest investigations show that pimaric acid consists of three isomerides (B. **19**, 2167).

Gum lac, obtained from East India fig trees, constitutes what is known as shellac when fused. This is employed in the preparation of sealing-wax and varnishes.

Amber is a fossil resin, found in peat-bogs. It consists of succinic acid, two resin acids, and a volatile oil. After fusion it dissolves easily in alcohol and turpentine oil, and serves for the preparation of varnishes.

To the *gum resins*, occurring mixed with vegetable gums, and gum in the juice of plants, belong gamboge, euphorbium, asafœtida, caoutchouc, and gutta percha.

Caoutchouc, because of its wide applicability, is especially important. It has been obtained from tropical Euphorbiaceæ, Apocinaceæ, etc. In Brazil it is made from *Siphonia elastica*, in India from *Ficus elastica*, as well as other varieties of Ficus. Purified caoutchouc has the formula (C_5H_8) x. When distilled it yields isoprene, C_5H_8 (see this), which polymerizes spontaneously to caoutchouc and also to dipentene. Caoutchouc takes up sulphur when it is thoroughly kneaded with it, or when it is treated with a mixture of S_2Cl_2 and CS_2 (B. **27**, R. 204, 521, 601, 609, 701, 816; **29**, R. 136).

The product is a vulcanized caoutchouc, which continues elastic within a considerable range of temperature.

AROMATIC HYDROCARBONS CONTAINING SEVERAL NUCLEI.

A. PHENYLBENZENES AND POLYPHENYL-FATTY HYDROCARBONS.

Just as alkyl groups are joined to one another, or as they are introduced into benzene and its homologues, so the benzene hydrogen atoms can be replaced by phenyl-, tolyl-, benzyl-, and other hydrocarbon residues. The products are: (1) The phenylbenzenes, in which the benzene nuclei are in immediate union:

$C_6H_5 . C_6H_5$	$C_6H_5 . C_6H_4 . CH_3$	$C_6H_4(C_6H_5)_2$	$C_6H_3(C_6H_5)_3$
Diphenyl	Phenyl Tolyl	Diphenyl Benzenes	Triphenyl Benzenes.

(2) The polyphenyl paraffins, olefines, and acetylenes, in which the benzene residues are held together by fatty hydrocarbons:

$C_6H_5 \searrow$ $\quad CH_2$ $C_6H_5 \nearrow$	$(C_6H_5)_3CH$	$C_6H_5 . CH_2$ $\vert$ $C_6H_5 . CH_2$	$C_6H_5 . CH$ $\Vert$ $C_6H_5 . CH$	$C_6H_5 . C$ $\equiv$ etc. $C_6H_5 . C$
Diphenyl-methane	Triphenyl-methane	Dibenzyl	Stilbene	Tolane.

In addition to these groups we have: B. *The aromatic hydrocarbons with condensed nuclei.*

I. PHENYLBENZENE GROUP.

I A. **Diphenyl Group.**—The first or parent hydrocarbon of this group is diphenyl or phenylbenzene.

Diphenyl, *Phenylbenzene, Biphenyl,* $C_6H_5 . C_6H_5$, melting at 71° and boiling at 254°, is present in slight amount in coal tar. It is formed (1) upon conducting benzene vapors through tubes heated to redness (Berthelot, Z. f. Ch., 1866, 707; B. **9**, 547; A. **230**, 5); (2) in the action of sodium upon the solution of brombenzene in ether or benzene—higher, condensed hydrocarbons being produced at the same time (Fittig, A. **121**, 363; B. **29**, 115); (3) from diazobenzene chloride (a) by action of benzene and aluminium chloride, (b) with stannous chloride, (c) when alcohol and Cu-powder act upon diazobenzene sulphate, (d) from the latter salt and warm benzene (B. **23**, 1226; **26**, 1997).

If dissolved in glacial acetic acid and oxidized with chromic anhydride it yields benzoic acid. Metallic sodium reduces diphenyl, dissolved in amyl alcohol, to *tetra-hydrodiphenyl,* $C_{12}H_{14}$, boiling at 245°. The latter readily forms a dibromide which alcoholic potash converts into *dihydro-diphenyl,* $C_{12}H_{12}$, boiling at 248° (B. **21**, 846). A dihydrodiphenyl of melting point 66° has been obtained from phenyldihydroresorcinol (p. 297) by converting this diketone into the corresponding dihydric alcohol, and removing two molecules of water from the latter by means of phosphorus pentoxide (A. **289**, 168). Fluorene (B. **19**, R. 672) is formed when methylene chloride and aluminium chloride act upon diphenyl.

Alkylic Diphenyls have been obtained: (1) by the action of nitrous acid upon the alcoholic solution of their amido-compounds (B. **17**, 468; **21**, 1096; (2) from the action of sodium upon the brominated alkylbenzenes (B. **4**, 396); (3) from diphenyl, chlor-alkyl,

or ethylene and aluminium chloride (B. **20**, R. 218); (4) from aromatic diazochlorides containing one nucleus (see p. 106). The position of the alkyl-groups is determined by oxidation, if it has not been made evident by the components.

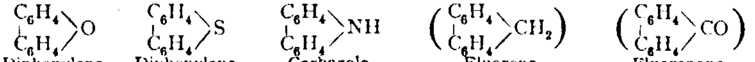
m-**Phenyltolyl**, m-*Methyl Diphenyl*, ...	boils at 272–277°.
p-**Phenyltolyl** (B. **26**, 1996) (m. p. + 3°), ...	" 263–267°.
m-**Ethyl Diphenyl**, ...	" 283°.
m_2-**Ditolyl**, m,m-Dimethyl Diphenyl (B. **25**, 1032),	" 286°.
o,m-**Ditolyl**, ...	" 286°.

p_2-**Ditolyl** (B. **29**, 114), m. p. 121°, is volatile without decomposition.

Diphenyl Substitution Products.—Each monosubstitution product of diphenyl can exist theoretically in three isomeric forms. Chlorine, bromine, the NO_2-group, and the sulpho-group prefer the p-position with reference to the point of union of the two benzene residues. o- and o,p-Derivatives are formed together with the p- and p_2-derivatives. The p_2-derivatives, having two different substituents,—*e. g.*, p-brom-p-nitro-diphenyl,—yield both p-brom- and p-nitrobenzoic acids when they are oxidized (see benzidine). The amidodiphenylenes, particularly benzidine, or p_2-diamidodiphenyl and the diphenyl sulphonic acids, afford, as in the case of the corresponding benzene derivatives, numerous derivatives of diphenyl.

It is interesting to note that o_2-disubstitution products are known in which a bivalent atom, O and S, or a bivalent group, NH, (CH_2, CO), replaces two hydrogen atoms in the ortho-position with reference to the point of union of the two benzene nuclei.

The principal representatives of such diphenylene compounds are:



Diphenylene Oxide — Diphenylene Sulphide — Carbazole — Fluorene — Fluorenone.

The first three will be treated in connection with the heterocyclic derivatives after furfurane, thiophene, and pyrrol, from which they can also be derived. They are formed by pyro-reactions from phenyl ether, phenyl sulphide, and diphenylamine.

Halogen Diphenyls.—o- and p-**Chlordiphenyl** melt at 34° and boil at 267°, and at 75° and at 282°. o- and p-**Bromdiphenyls**, liquid, boil at 297° and melts at 89°, and boils at 310°. p_2-**Dichlor-**, p_2-**Dibrom-**, and p_2-**Di-ioddiphenyls** melt at 148° and boil at 315°, at 164° and 357°, and melt at 202° (A. **207**, 333).

Perchlordiphenyl, $C_{12}Cl_{10}$, does not melt at 270°. It is often produced in exhaustive chlorinations (B. **16**, 2881).

Nitro-diphenyls.—The nitration of diphenyl gives rise to o- and p-nitro-, as well as to p_2- and o,p-dinitrodiphenyls. o_2- and m_2-Dinitro-diphenyls are obtained from benzidine (B. **20**, 1028). o- and p-**Nitro-diphenyls** melt at 37° and boil at 320°; at 113° and at 340°.

o_2-, m_2-, p_2-, and o,p-**Dinitro-diphenyls** melt at 124°, 197°, 233°, and 93°. p_2- and o,p-Dinitro-diphenyl have also been obtained from sodium isodiazonitrobenzene and nitrobenzene (B. **29**, 165). p-**Brom-p-nitro-diphenyl** melts at 173° (A. **174**, 218).

Amido-diphenyls and **Amido-ditolyls** can be prepared by the reduction of the corresponding nitro-compounds. The formation of p_2-diamido-diphenyl by the rearrangement of its isomeride hydrazobenzene (p. 117) is of great technical importance, because p_2-diamido-diphenyl or benzidine is a starting-out substance for the preparation of substantive cotton dyes—dyes which unite directly with the cotton fiber without the aid of mordants.

o-**Amido-diphenyl**, melting at 45°, is also obtained from o-phenylbenzamide by means of bromine and caustic soda (A. **279**, 266; B. **25**, 1974). When conducted over heated lime it forms *carbazole*. p-**Amido-diphenyl**, *Xenylamine*, melts at 51°

and boils at 322° (A. **260**, 233). p_2-**Nitroamido-diphenyl,** from p_2-dinitro-diphenyl, melts at 198°.

o_2-**Diamido-diphenyl,** melting at 81°, and m_2-**Diamido-diphenyl** have been obtained by reducing o_2- and m_2-dinitro-diphenyl. When o_2-diamido-diphenyl is heated with concentrated sulphuric acid it yields *carbazole*. Its tetrazochloride is changed by potassium sulphydrate to *carbazole*, and when its aqueous solution is heated *diphenylene oxide* is produced (B. **26**, 1703). The reduction of the *tetrazo*-compound of o_2-diamido-diphenyl gives rise to **Diphenylene** o_2-**dihydrazine,** $\begin{matrix} C_6H_4[2]NHNH_2 \\ | \\ C_6H_4[2']NHNH_2 \end{matrix}$, melting at 110° (B. **29**, 2270). When heated with hydrochloric acid at 150° it breaks down easily into ammonium chloride and an o_2-*azodiphenylene*, so called **phenazone,**

$C_6H_4\langle \overset{N = N}{\rule{3em}{0.4pt}} \rangle C_6H_4$, which can also be directly obtained by the reduction of o_2-dinitro-diphenyl with sodium amalgam and methyl alcohol.

Phenazone will be treated at the conclusion of the ortho-diazines under the heterocyclic compounds.

Benzidine, p_2-*Diamido-diphenyl,* melting at 122° (Zinin, 1845), is obtained by the reduction of p_2-dinitro-diphenyl and p_2-nitroamido-diphenyl. It is technically prepared by the reduction of azobenzene in acid solution; the hydrazobenzene, formed at first, rearranges itself to benzidine and diphenyl, or o,p-diamido-diphenyl. This is a remarkable reaction, to which attention has already been called in connection with hydrazobenzene (p. 117) (A. **207**, 330).

The great insolubility of the sulphate in water affords a means of separating benzidine from diphenyline. When treated with concentrated sulphuric acid and nitric acid, one or two NO_2-groups enter in the m position with reference to the amido-groups of benzidine. The products are o-nitro-p_2-diamido-diphenyl and o_2-dinitro-p_2-diamido-diphenyl (B. **23**, 794). m_2-Dinitro-p_2-diacetamido-diphenyl results on nitrating diacetbenzidine. The two nitro-compounds by removal of the amido-groups yield o_2- and m_2-dinitro-diphenyls (see these).

Constitution.—The p-position of the two amido-groups of benzidine (1) is evident from the oxidation of p_2-bromnitro-diphenyl to p-brom- and p-nitrobenzoic acids (5, 6), because benzidine (1) is formed from p_2-dinitro-diphenyl (2), which may be rearranged to p_2-amidonitro-diphenyl (3), and p_2-bromnitro-diphenyl (4) (Gustav Schultz, A. **174**, 227):

$$\underset{(1)}{\begin{matrix} C_6H_4[4]NH_2 \\ | \\ C_6H_4[4]NH_2 \end{matrix}} \longrightarrow \underset{(2)}{\begin{matrix} C_6H_4[4]NO_2 \\ | \\ C_6H_4[4]NO_2 \end{matrix}} \longrightarrow \underset{(3)}{\begin{matrix} C_6H_4[4]NO_2 \\ | \\ C_6H_4[4]NH_2 \end{matrix}} \longrightarrow \underset{(4)}{\begin{matrix} C_6H_4[4]NH_2 \\ | \\ C_6H_4[4]Br \end{matrix}} \longrightarrow \left[\begin{matrix} \to \begin{matrix} C_6H_4[4]NO_2 \\ | \\ CO_2H \end{matrix} \ (5) \\ \to \begin{matrix} CO_2H \\ | \\ C_6H_4[4]Br \end{matrix} \ (6) \end{matrix} \right.$$

The constitution of benzidine forms the basis for *one* of the proofs of the constitution of diphenic acid (p. 340); also for that of phenanthrene isomeric with anthracene.

Benzidine Disulphate consists of small scales with a silvery luster; preparation, B. **26**, R. 321. Concentrated sulphuric acid converts it into benzidine sulphone (B. **22**, 2467).

Diacetbenzidine melts at 317°. **Thionylbenzidine,** $(C_6H_4 . NSO)_2$ (B. **24**, 753). **Di-(o-nitrobenzyl)-benzidine** melts at 227° with decomposition (B. **29**, 1450).

o-Nitro-p_2-diamido-diphenyl, m-Nitrobenzidine, melts at 143° (B. **23**, 796)—see benzidine.

o_2-**Dinitro-p_2-diamido-diphenyl,** m-*Dinitrobenzidine,* melts at 214° (B. **23**, 795). 3_2-**Dinitro-4_2-diacetdiamido-diphenyl** melts above 300° and is converted by caustic potash into 3_2-**dinitro-4_2-diamido-diphenyl,** o-*dinitrobenzidine,* melting at 220° (B. **5**, 237; **20**, 1024). 5_2-**Dinitro-2_2-diamido-diphenyl** (B. **25**, 128).

o,p-Diamido-diphenyl, *Diphenyline*, melts at 45° and boils at 362°. Preparation, see benzidine (A. 207, 348; B. 22, 3011). **o,p_2-Triamido-diphenyl**, m-*Amidobenzidine*, (B. 23, 797). **o_2,p_2-Tetramido-diphenyl**, m_2-*diamidobenzidine*, melting at 165°, is obtained from o_2-dinitro-p_2-diamido-diphenyl (see benzidine), and by loss of ammonia becomes p_2-diamido-carbazole.

Di-p-phenylenediamine, $(NH_2)_2[2,5]C_6H_3 . C_6H_3[2,5](NH_2)_2$, melting at 168°, is converted by hydrochloric acid at 180° into 5_2-diamido-carbazole (B. 25, 131).

Benzidine Homologues, p_2 Diamidophenyl-tolyl, o-Methyl Benzidine, $H_2N . C_6H_4 . C_6H_3(CH_3) . NH_2$, is formed upon reducing a mixture of nitrobenzene and o-nitrotoluene. It melts at 90° (B. 23, 3222).

o-**Tolidine**, p_2-*Diamido*-m_2-*dimethyldiphenyl*, from o-hydrazotoluene, melts at 128° (B. 20, 2017; 23, 3252).

m-**Tolidine**, p_2-*Diamido*-o_2-*dimethyldiphenyl*, from m-hydrazotoluene (p. 117), melts at 109°. Isomeric *ditolylin* (B. 23, 3252) is produced at the same time.

o- and m-Hydrazotoluenes suffer under the influence of acids the *benzidine rearrangement*. p-Hydrazotoluene under like conditions follows the *semidine rearrangement* (p. 118).

Benzidine Dyes.—*Benzidine* yields azo dyes, transposition products of the diazochloride from benzidine and amidosulphonic acids, phenol carboxylic acids, and phenolsulphonic acids, which unite directly with cotton fiber (Griess, B. 22, 2469). These dyes are obtained as sodium salts, which are prepared by adding the aqueous solution of the tetrazochloride to the aqueous solution of two molecules of the sodium salt of the other component.

Sodium acetate, sodium carbonate, or ammonia is added to the solution of the sodium salt to combine the hydrochloric acid which is liberated:

$$\begin{matrix} C_6H_4N_2.Cl \\ | \\ C_6H_4N_2.Cl \end{matrix} + \begin{matrix} C_6H_4(OH)CO_2Na \\ \\ C_6H_4(OH)CO_2Na \end{matrix} + CO_3Na_2 = \begin{matrix} C_6H_4N:N.C_6H_3(OH).CO_2Na \\ | \\ C_6H_4N:N.C_6H_3(OH).CO_2Na \end{matrix} + 2HCl + CO_2 + H_2O.$$

The sodium salts of two different components can be, step by step, brought into reaction with the tetrazochloride, and *mixed* tetrazo-dyes (B. 19, 1697, 1755; 20, R. 273; 21, R. 71) result.

Representatives of the class of benzidine dyes are:

Chrysamine, Flavophenine, $\begin{matrix} C_6H_4 . N:N . C_6H_3(OH) . CO_2Na \\ | \\ C_6H_4 . N:N . C_6H_3(OH) . CO_2Na \end{matrix}$, which is made from diphenyltetrazochloride and sodium salicylate (equation above) (B. 22, 2459).

Congo Yellow, $\begin{matrix} C_6H_4 . N:N . C_6H_3(NH_2) . SO_3Na \\ | \\ C_6H_4 . N:N . C_6H_4 . OH \end{matrix}$, is obtained from diphenyl tetrazochloride, phenol, and sulphanilic acid.

The preceding dyes color cotton fiber yellow.

The first red dye brought into commerce was *Congo red*, which is formed from the interaction of diphenyltetrazochloride and sodium naphthionate. It will be brought forward again under the naphthalene azo-dyes. The β naphthylamine sulphonic acids are particularly valuable in the preparation of substantive dyes.

Substantive dyes, similar to those from benzidine, have been obtained from p_2-amido-methyldiphenyl, o-*methylbenzidine*, o- and m-*tolidines*, dianisidine (p. 337), *thiobenzidine, thiotolidine* (B. 20, R. 272), p_2-diamido-benzophenone (p. 347), p_2-*diamido-stilbene* (p. 370) (B. 21, R. 383).

It may be said that, *as a rule*, those *substituted* benzidines (nitro and sulphobenzidines, tolidines, etc.) having the substituent in the meta-position (relative to the amido-group) yield *inactive* or *feeble substantive* azo-dyes. Diamido-diphenylene oxide, benzidine sulphone (see this), and diamido carbazole (see this) constitute exceptions. They contain a third ring-shaped chain (B. 23, 3252, 3268; 24, 1958).

It is interesting to observe that benzidine hydrochloride itself unites with cotton. It mordants the cotton. Hence it is possible to produce the benzidine upon the fiber (B. 19, 2014).

The "*one-sided diazotizing*" of benzidine is attained through the action of a p-tetrazo-diphenyl salt upon the aqueous solution of a benzidine salt (B. 27, 2627); compare

migrations of the diazo-group, p. 100. When the bisdiazocompound of benzidine is allowed to act upon acetoacetic ester there result, with one molecule of the ester: **Cycloformazylcarboxylic Ester**, $COOC_2H_5C\begin{cases} N.NH-C_6H_4 \\ N:N-C_6H_4 \end{cases}$ (the two C_6H_4 groups joined), a reddish-brown powder, fusing with difficulty (see formazyl carboxylic acid, p. 130); and with two molecules of the ester:

Bisacetylglyoxylic Ester Phenylhydrazone, $[CH_3COC(CO_2C_2H_5):NNHC_6H_4-]_2$, yellow needles, melting at 198° (A. **295**, 332).

p-**Hydrazinodiphenyl**, $C_6H_5C_6H_4[4]NH.NH_2$ (B. **27**, 3105).

Biphenylsulphonic Acids.—On digesting biphenyl with sulphuric acid the first product is **biphenyl-p-sulphonic acid** (its *chloride* melting at 115° and its *amide* at 229°), and later **biphenyl-p$_2$-disulphonic acid**, melting at 72°, and its *chloride* at 203° (B. **13**, 288). When potassium biphenyl-p-sulphonate is heated it changes to biphenyl and potassium biphenyl-p$_2$-disulphonate. **Biphenyl-o$_2$ disulphonic Acid** is obtained from benzidine-o$_2$-disulphonic acid (A. **261**, 310).

Benzidine Sulphonic Acids: 4$_2$-**Diamido-biphenyl-2$_2$-disulphonic Acid** is formed from m-hydrazobenzene sulphonic acid (A. **261**, 310; **268**, 130), and when fused with caustic potash yields 4$_2$-diamido diphenylene oxide.

4$_2$-**Diamido-biphenyl-3$_2$-disulphonic Acid** is produced on heating benzidine with ordinary sulphuric acid to 210° (B. **22**, 2466).

o-**Tolidine Disulphonic Acid**, 4$_2$-*Diamido-5$_2$-dimethylbiphenyl-2$_2$-disulphonic Acid* (A. **270**, 359).

4$_2$-**Dihydrazino-biphenyl-2$_2$-disulphonic Acid**, $\left(C_6H_3\begin{matrix} N_2H_3 \\ SO_3H \end{matrix}\right)_2$. See A. **261**, 323.

Oxybiphenyls are obtained from the biphenyl derivatives by methods similar to those by which the phenols themselves are prepared from the benzene derivatives, and also in the oxidation of phenols containing a single nucleus, when they are fused with caustic potash (B. **27**, 2107).

Monoxybiphenyls.—p-**Oxybiphenyl**, $C_6H_5.C_6H_4[4]OH$, melting at 165° and boiling at 306°, is obtained from diazobenzene chloride and phenol (B. **23**, 3708).

Dioxybiphenyls.—o$_2$-**Dioxybiphenyl**, o$_2$-*Biphenol*, melting at 98°, is made on fusing fluorene (see this) with caustic potash at 400°, and from biphenyl-o$_2$-disulphonic acid (A. **261**, 362). m-**Biphenol**, melting at 123.5°, is obtained from o-*dianisidine* and m$_2$-diamidobiphenyl (B. **27**, 2107). p$_2$-**Biphenol**, melting at 272°, is prepared from benzidine, biphenyl-p$_2$-disulphonic acid, and from phenol by the action of $KMnO_4$ (B. **25**, R. 335). o,p-**Biphenol**, from diphenyline, melts at 160°.

Tetraoxybiphenyls.—**Bipyrocatechine**, $(HO)_2C_6H_3.C_6H_3(OH)_2$, melting at 84°, **Biresorcinol**, melting at 310°, and **bihydroquinone**, melting at 237°, result when the three dioxybenzenes are fused with sodium hydroxide (B. **11**, 1336; **12**, 503; **18**, R. 23).

Hexaoxybiphenyls.—Hydrocoerulignone is a derivative of hexaoxybiphenyl. Coerulignone, or cedriret, bears the same relation to it as quinone to hydroquinone.

Coerulignone, $O_2:C_{12}H_6(OCH_3)_4$, separates as a violet powder when crude wood-spirit is purified on a large scale by means of potassium chromate. It is further formed on oxidizing dimethyl-pyrogallol (p. 164) with potassium chromate or ferric chloride:

$$2C_6H_3\begin{cases}(O.CH_3)_2 \\ OH\end{cases} \xrightarrow{-4H} \begin{matrix}(CH_3O)_2:C_6H_2O \\ | \\ (CH_3O)_2:C_6H_2O\end{matrix}$$

Coeruligone is insoluble in the ordinary solvents, and is precipitated in fine, steel-blue needles, from its phenol solution, by alcohol or ether. It dissolves in concentrated sulphuric acid with a beautiful blue color. Large quantities of water color the solution red at first. Reducing agents (tin and hydrochloric acid) convert coerulignone into colorless hydrocoerulignone, which changes again to the first by oxidation. Coerulignone is, therefore, a quinone body, and may be called a *double-nuclei quinone.*

It unites with primary aromatic amines, forming blue dyes. It is very probable that in doing this two methoxyl groups are replaced by amino-residues (B. **30**, 235).

Hydrocoerulignone, $C_{16}H_{18}O_6$, melts at 190°, and distils with almost no decompo-

sition. When heated with concentrated hydrochloric acid it breaks down into methyl chloride and **Hexaoxydiphenyl**, $C_{12}H_{10}O_6$ (B. **11**, 797).

Amido-oxybiphenyls are obtained from oxybiphenyls (B. **22**, 335), and from the alkyl ethers of oxyazoderivatives, having free p-positions, by the benzidine rearrangement (B. **23**, 3256). In the coal-tar industry o-**dianisidine** or 4_2-**diamido**-3_2-**dimethoxybiphenyl** and **ethoxybenzidine**, from o-nitroanisol, are of great value. They yield violet, blue, and black substantive cotton dyes with amidonaphthalene sulphonic acid, naphthol sulphonic acid, and amidonaphthol sulphonic acids: *azoviolet*, *benzazurine*, *diamine black*, etc. (B. **22**, R. 372; **24**, R. 55, 56, etc.).

Biphenyl Carboxylic Acids are obtained from diphenyl derivatives by reactions similar to those by which the benzene carboxylic acids are prepared from the derivatives of benzene. They are of just as much importance in determining the constitution of diphenyl bodies as the benzene-carboxylic acids for the benzene compounds.

Biphenyl Monocarboxylic Acids.—There are three possible acids: o-**Phenyl-benzoic Acid**, $C_6H_5 . C_6H_4[2]CO_2H$, melting at 111°, is produced by fusing diphenylene ketone with caustic potash (A. **166**, 374); by the distillation of sodium salicylate with triphenyl phosphate (J. pr. Ch. [2], **28**, 305); and from o-amido- and o-methyl-diphenyl. If the acid be treated with PCl_5, or if it be heated with sulphuric acid to 100°, or with lime to more elevated temperatures, diphenylene ketone will be formed (A. **266**, 142; **279**, 259). m-**Phenyl-benzoic Acid**, melting at 160°, results from the oxidation of m-methylbiphenyl, of isodiphenylbenzene (see this), and in the reduction of brom-m-phenylbenzoic acid (B. **27**, 3390).

p-**Phenyl-benzoic Acid**, melting at 218°, is obtained from p-methylbiphenyl, from p-diphenylbenzene, from sodium biphenylsulphonate (A. **282**, 143), from p-amidodiphenyl, and by fusing benzoic acid with caustic potash. It is reduced to *p-phenylhexahydrobenzoic acid*, $C_6H_5C_6H_{10}[4]CO_2H$, melting at 202°, which upon heating to 100° with hydrochloric acid is rearranged to *phenylisohexahydrobenzoic acid*, melting at 113° (A. **282**, 139). p_2-**Nitrophenylbenzoic Acid**, melting at 222–225°, results from the oxidation of p_2-nitrophenyl tolyl. It yields the corresponding *amido-acid* (B. **29**, 166) on reduction.

Oxybiphenyl Carboxylic Acids.—The following acids are all derivatives of o-phenylbenzoic acid.

6-**Phenyl-salicylic Acid**, $C_6H_5[6]C_6H_3[2](OH)CO_2H$, melting at 159°, results upon fusing 3-oxydiphenylene ketone and potassium hydroxide (B. **28**, 112).

2-**Phenyl-m-oxybenzoic Acid**, $C_6H_5[2]C_6H_3[3]OH . CO_2H$, melting at 154°, is obtained, together with [*biphenylmethylolid*], as the principal product in the fusion of 6-oxydiphenylene ketone with potassium hydroxide (A. **284**, 307).

o-**Oxyphenyl-o-benzoic Acid** is only known in the form of its lactone, [biphenylmethylolid], $\begin{matrix} C_6H_4[2]CO \\ | \qquad | \\ C_6H_4[2]O \end{matrix}$, melting at 92.5°, which is formed as a by-product on fusing 6-oxydiphenylene ketone or o-oxyfluorenone with caustic potash, in small quantities by the action of $POCl_3$ upon sodium salicylate, and when phenol acts upon the sulphate of o-diazobenzene (A. **284**, 316). It corresponds in composition to *phenanthridone*, $\begin{matrix} C_6H_4[2]CO \\ | \qquad | \\ C_6H_4[2]NH \end{matrix}$, melting at 293° (see this), which is produced when bromine and caustic potash act upon diphenamic acid (A. **276**, 245).

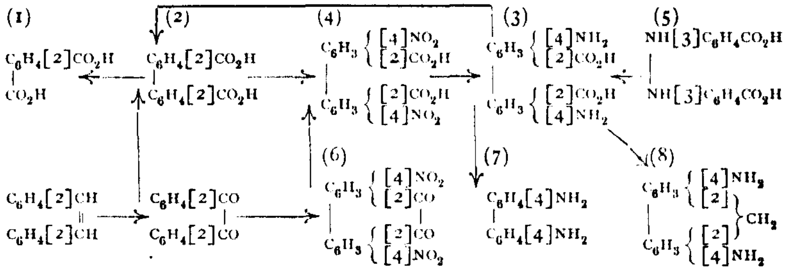
o-**Oxyphenyl-o-benzoic Acid**, $HO[4]C_6H_4[1]C_6H_4[2]CO_2H$, melting at 206°, is produced, together with [biphenylmethylolid] and phenyl-ether salicylic acid, by the action of phenol upon the sulphate of o-diazobenzoic acid (A. **286**, 323).

Biphenyl Dicarboxylic Acids contain the two CO_2H-groups, either linked to the same or to different benzene residues. *Diphenic acid* is the most important biphenyl dicarboxylic acid.

[5]-**Phenylisophthalic Acid**, $C_6H_5[5]C_6H_3[1,3](CO_2H_2)$, melts above 310°, and is formed on boiling benzaldehyde and pyroracemic acid with baryta-water (B. **24**, 1750).

Diphenic Acid, o_2-*Biphenyldicarboxylic Acid*, $CO_2H[2]C_6H_4 . C_6H_4[2]CO_2H$, melts at 229°. It is produced in the oxidation of phenanthraquinone with a chromic acid mixture, or by boiling it with alcoholic potash. The constitution of phenanthrene

follows from its constitution. That of diphenic acid (2) is evident from its oxidation to o-phthalic acid (1) (Anschütz and Japp, B. **11**, 211) by potassium permanganate, and its formation by the deamidation of p_2-diamido-diphenyl-o_2-dicarboxylic acid (3), which is obtained on the one hand from p_2-dinitrodiphenic acid (4), and on the other by the rearrangement of m-hydrazobenzoic acid (5) (G. Schultz, A. **204**, 95):



In this circle of reactions there should also be included the formation of p_2-dinitrodiphenic acid by the oxidation of p_2-dinitrophenanthraquinone (6) and the transposition of diamidodiphenic acid to benzidine (7), the constitution of which was previously deduced (p. 337), and to p_2-diamido-fluorene (8).

Concentrated sulphuric acid changes diphenic acid to diphenylene-ketone carboxylic acid (see this). When it is digested with acetyl chloride or acetic anhydride it yields **Diphenic Anhydride,** $\begin{matrix} C_6H_4 . CO \\ | \\ C_6H_4 . CO \end{matrix} > O$, melting at 213° (A. **226**, 1). This is a remarkable compound, inasmuch as it can be viewed as adipic anhydride and contains a "seven-membered" ring. **Diphenic Chloride,** $\begin{matrix} C_6H_4 . COCl \\ | \\ C_6H_4 . COCl \end{matrix}$, melting at 93°, is reduced in ethereal solution by zinc and hydrochloric acid to phenanthrene hydroquinone, $\begin{matrix} C_6H_4 . C(OH) \\ | \quad \| \\ C_6H_4 . C(OH) \end{matrix}$ (A. **247**, 268). **Diphenamino-acid,** $\begin{matrix} C_6H_4 . CO . NH_2 \\ | \\ C_6H_4 . CO . OH \end{matrix}$, melting at 193°, is converted by a hypobromite or hypochlorite, in alkaline solution, into phenanthridone (see this) (A. **276**, 248). **Diphenimide,** $\begin{matrix} C_6H_4 . CO \\ | \\ C_6H_4 . CO \end{matrix} > NH$, melts at 219° (A. **247**, 271).

p_2-Dinitrodiphenic Acid, $\begin{matrix} NO_2[4]C_6H_3[2]CO_2H \\ | \\ NO_2[4]C_6H_3[2]CO_2H \end{matrix}$, melts at 253°. See diphenic acid for its formation.

p_2-Diamidodiphenic Acid—for its formation and decomposition see diphenic acid.

Isodiphenic Acid (o,m′) $CO_2H[3]C_6H_4 . C_6H_4[2]CO_2H$, melting at 216°, is produced when diphenyleneketone carboxylic acid (see this) is fused with caustic potash.

o,p′-Biphenyldicarboxylic Acid, $CO_2H[4]C_6H_4 . C_6H_4[2]CO_2H$, melting at 251°, is obtained from diphenyline (p. 338) (B. **22**, 3019).

p_2-Biphenyldicarboxylic Acid decomposes at a more elevated temperature. It is obtained from diphenyl-p_2-dicyanide and by oxidizing p_2-ditolyl.

p_2-Diamidobiphenyl-m_2-dicarboxylic Acid is obtained from o-nitrobenzoic acid, just as p_2-diamidodiphenic acid is prepared from m-nitrobenzoic acid (B. **25**, 2797).

m_2-Dimethyl-biphenyl-p_2-dicarboxylic Acid melts above 300°, is formed from o-tolidine (p. 338) and is oxidized to **diphthalic acid,** *biphenyl-m_2,p_2-dicarboxylic acid,* $(CO_2H)_2[3,4]C_6H_3 . C_6H_3[3,4](CO_2H)_2$ (B. **26**, 2486).

I B. Diphenylbenzenes, *Diphenylphenylenes,* $C_6H_4(C_6H_5)_2$.—Two such bodies are known: **m-Diphenylbenzene,** *Isodiphenylbenzene,* melting at 85° and boiling at 369°, and **p-Diphenylbenzene,** melting at 205° and boiling at 383°. They are formed simultaneously on conducting benzene through a tube heated to redness, and by the action of diazobenzene chloride upon diphenyl and Al_2Cl_6 (B. **26**, 1998). The p-body is also

produced in the action of sodium upon a mixture of p-dibrombenzene and brombenzene (A. **164**, 168). Isodiphenylbenzene is also prepared from m-dichlorbenzene and chlorbenzene by the action of sodium in xylene (B. **29**, R. 773).

I C. **Triphenyl Benzenes,** $C_6H_3(C_6H_5)_3$.—The symmetrical or [1,3,5] modification is formed from acetophenone when heated with P_2O_5, or by conducting hydrochloric acid gas into it, just as mesitylene is obtained from acetone (p. 214). It melts at 169° (B. **23**, 2533). [1,2,3] (?)-**Triphenyl Benzene** melts at 157° (B. **26**, 69).

II. BENZYLBENZENE GROUP.

Benzylbenzene or diphenyl methane is the simplest hydrocarbon of this group. The alkyl diphenylmethanes, and the compounds substituted in the benzene residues by the NO_2, NH_2, or OH-groups, are derived from it. If we suppose an hydrogen atom of the CH_2-group to be replaced by OH, we obtain the formula of benzhydrol or diphenylcarbinol, which changes by oxidation to benzophenone or diphenylketone. Diphenylmethane, $CH_2(C_6H_5)_2$, benzhydrol, $HOCH(C_6H_5)_2$, and benzophenone, $CO(C_6H_5)_2$, are the simplest representatives of the hydrocarbons, the secondary alcohols and the ketones of this group. Attached to them are the corresponding carboxylic acids—*e. g.*:

$CH_2<^{C_6H_4 . CO_2H}_{C_6H_5}$	$CH(OH)<^{C_6H_4CO_2H}_{C_6H_5}$	$CO<^{C_6H_4CO_2H}_{C_6H_5}$
Benzyl-benzoic Acid	*Benzhydrol-benzoic Acid*	*Benzoyl-benzoic Acid.*

1. HYDROCARBONS (DIPHENYL METHANES).

Formation.—(1) From benzyl chloride, benzene and zinc-dust (Zincke, A. **159**, 374), or aluminium chloride (Friedel and Crafts). (2) From formaldehyde, methylal, or methylene diacetate with benzene and sulphuric acid (Baeyer, B. **6**, 963). Both reactions are capable of wide generalization. Thus, by use of the second reaction, substituting other aldehydes for formaldehyde, numerous hydrocarbons have been obtained in which two benzene residues are attached to the same carbon atom (see unsym. diphenyl-ethane, p. 368).

Both reactions, upon substituting phenol ethers or dialkyl anilines for benzene, lead to RO- and R_2N-substitution products.

(3) Aromatic alcohols condense with aromatic hydrocarbons to benzyl benzenes—*e. g.*, benzyl alcohol and benzene yield diphenyl methane (B. **6**, 963).

(4) By the reduction of ketones, into which the benzyl benzenes are oxidized.

Diphenyl Methane, $C_6H_5 . CH_2 . C_6H_5$, *Benzyl Benzene*, is obtained (1) from benzyl chloride and benzene with zinc-dust or $AlCl_3$; (2) from CH_2Cl_2 with benzene and $AlCl_3$; (3) from methylal, or (4) from benzyl alcohol, benzene, and sulphuric acid; (5) by the reduction of benzophenone with zinc-dust, or zinc and sulphuric acid, or hydriodic acid and phosphorus, and (6) upon distilling diphenylacetic acid (p. 368) with soda-lime (A. **155**, 86).

Diphenyl methane possesses the odor of oranges. It melts at 26.5° and boils at 261°. When conducted through ignited tubes it yields diphenylene methane or fluorene; a chromic acid mixture oxidizes it to benzophenone, whereas concentrated nitric acid changes it to p_2-, o,p-dinitro- and tetranitrodiphenylmethane (A. **283**, 154).

Benzyl Toluenes, *Phenyl Tolyl Methanes*, $C_6H_5 . CH_2 . C_6H_4 . CH_3$.—A liquid mixture of o- and p-benzyl toluene, which cannot be separated, is obtained by the action of zinc-dust on a mixture of benzyl chloride and toluene. Anthracene is formed at the same time. The pure *para*-body has been formed by heating para-phenyl tolyl ketone with zinc-dust, and is a liquid, boiling at 285°. It appears also to be produced in the action of sodium upon p-bromtoluene along with p-ditolyl (p. 336). Brommesitylene and sodium yield, together with dimesityl, a *pentamethyldiphenyl methane* (B. **29**, 111).

Benzyl-p-xylene boils at 294°. **Benzyl Mesitylene** melts at 36° and boils at 301°. The **benzyl durenes** melt at 60° and boil at 310°; and at 145° and 326°. **Benzyl Pentaethyl Benzene** melts at 88° (B. **26**, R. 58). p_2-**Ditolylmethane** melts at 22° and boils at 286°. **Dimesityl Methane** melts at 130°. The unsym. hydrocarbons were obtained according to methods 1 and 4, and the sym. according to method 1.

Nitrodiphenyl Methanes, $C_6H_5 . CH_2 . C_6H_4 . NO_2$ (A. **283**, 157).—The *ortho*-compound, prepared from o-nitrobenzyl chloride and benzene with $AlCl_3$, is liquid (B. **18**, 2402; **29**, 1303). The *meta*- and *para*-bodies are derived from meta- and para-nitrobenzyl alcohol by means of benzene and sulphuric acid. The first is an oil; the second melts at 31° (B. **16**, 2716).

m_2-**Dinitrodiphenyl Methane,** melting at 174°, is formed from m-nitrobenzyl alcohol with nitrobenzene, or from formaldehyde, nitrobenzene and concentrated sulphuric acid (B. **27**, 2293, 2321). m,p-**Dinitrodiphenyl Methane,** p-**Nitrobenzyl-m-nitrobenzene,** melts at 103°. p_2-**Dinitrodiphenyl Methane** melts at 183°. It is obtained from diphenyl methane along with o,p-dinitrodiphenyl methane, melting at 118° (B. **27**, 2110; A. **194**, 363).

Tetranitrodiphenyl Methane, melting at 172°, forms dark blue colored salts with alcoholic potash (B. **21**, 2475).

Amido-diphenyl Methanes.—o-**Amido-diphenyl Methane** is a liquid. When its vapors are conducted over ignited lead oxide, acridine (see this) results. Nitrous acid converts it into fluorene (B. **27**, 2786). m- and p-**Amido-diphenyl Methane** melt at 46° and 34° respectively (B. **16**, 2718).

p_2-**Diamido-diphenyl Methane,** melting at 85°, is also produced from methylene diphenylimide in the presence of hydrochloric acid or aniline hydrochloride by an intramolecular atomic displacement, which recalls the benzidine transposition and the formation of aniline homologues from the phenylalkylamines (p. 73). It changes completely to para-rosaniline or rosaniline when heated with aniline or o-toluidine in the presence of an oxidizing agent (B. **25**, 303).

Its *tetramethyl derivative* results from dimethyl aniline by means of $C_2H_2I_2$, CCl_3H, (or CCl_4), or with methylal, or by the action of CS_2 and zinc upon dimethyl aniline. It melts at 90°.

The hydrogen of the group CH_2 attached to *basic* radicals *is very readily replaced by sulphur;* see p_2-tetramethyl-diamidothiobenzophenone (p. 348). See A. **283**, 149, for isomeric *diamidodiphenyl methanes.*

Oxybenzyl Benzenes.—p-**Benzyl Phenol,** melting at 84° and boiling at 325° (in CO_2), is produced (1) from benzyl chloride, phenol, and zinc; (2) from benzyl alcohol, phenol with concentrated sulphuric acid, or zinc chloride; (3) from p-amido-diphenyl methane.

o_2-**Dioxydiphenyl Methane** is only known in the form of its anhydride, xanthene (see this).

p_2-**Dioxydiphenyl Methane** is produced on fusing diphenyl methane disulphonic acid with KOH (A. **194**, 318). It melts at 158°. Its *dimethyl ether* is formed from anisol and methylal by the action of concentrated sulphuric acid (B. **7**, 1200), and melts at 52°.

Methylene Dipyrocatechol, $CH_2[C_6H_3(OH)_2]_2$, melting with decomposition at 220°, is produced on boiling a solution of pyrocatechin and formaldehyde with hydrochloric acid or sulphuric acid (B. **26**, 254).

2. ALCOHOLS (BENZHYDROLS).

Diphenyl Carbinol, *Benzhydrol*, $(C_6H_5)_2CH.OH$, melts at 68° and boils at 298° with partial decomposition into water and *benzhydrol ether*, $[(C_6H_5)_2.CH]_2O$, melting at 199°. It is produced on heating diphenyl brom-methane with water to 150°; more readily from benzophenone with sodium amalgam, or by heating with alcoholic potassium hydroxide and zinc-dust (together with benzpinacone) (A. **184**, 174).

Phenyl-p-tolyl Carbinol melts at 52° (A. **194**, 265).

Diphenyl Carbinol Chloride, *Diphenyl Chlormethane*, melting at 14°, is obtained from benzhydrol and HCl. When heated it breaks down into HCl and tetraphenyl ethylene (p. 378) (B. **7**, 1128). *Diphenylbrom-methane*, from diphenylmethane and bromine, melts at 45°.

Benzhydrylamine, $NH_2.CH(C_6H_5)_2$, boiling at 288°, is obtained from diphenylbrommethane and from benzophenonoxime (B. **19**, 3233). The latter method has afforded the *homologous alkylbenzhydroxylamines* (B. **24**, 2797). The *formyl derivative*, from benzophenone and ammonium formate at 200–250° (B. **19**, 2129), melts at 132°. The *thionyl compound* boils at 88° (35 mm.) (B. **26**, 2189). *Dibenzhydrylamine* melts at 136°.

β-Benzhydrylhydroxylamine, [Diphenylaminol Methane], $HO.NH.CH(C_6H_5)_2$, melting at 78°, is formed on boiling a solution of diphenyl brom-methane and acetoxime with glacial acetic acid and water (A. **278**, 364).

o-Amidobenzhydrol, $C_6H_4{<}{}^{CH(OH)C_6H_5}_{NH_2}$, melting at 120°, is formed in the reduction of o-amidobenzophenone. It is capable, like o-amidobenzyl alcohol (p. 180), of producing heterocyclic compounds (B. **29**, 1304).

In the *aldol condensation* of benzaldehyde or p-nitrobenzaldehyde and dimethyl aniline with hydrochloric acid (by $ZnCl_2$ or oxalic acid the products are triphenylmethane derivatives) there arise:

p-Dimethyl Amidobenzhydrol, $C_6H_5CH(OH).C_6H_4N(CH_3)_2$, melting at 69°, and **p-Dimethylamido-p-nitrobenzhydrol,** melting at 96° (B. **21**, 3292). By reduction the latter compound yields p-*dimethyl-amido*-p-*amido-diphenylmethane*, melting at 165°. **p-Tetramethyl-diamido-benzhydrol,** melting at 96°, has been obtained by the reduction of p_2-tetramethyldiamidobenzophenone (B. **22**, 1879). On boiling the former with dilute mineral acids until the blue color has disappeared, it breaks down into dimethylaniline and dimethylamidobenzaldehyde (B. **27**, 3316). In the solid condition p_2-tetramethyldiamidobenzhydrol is white, while its solution is blue in color (B. **20**, 1733 Anm.).

3. KETONES (BENZOPHENONES).

The ketones of the benzylbenzene group bear the same relation to the benzoic acids that the acetones bear to the fatty acids:

$CH_3.CO_2H$	$CO{<}{}^{CH_3}_{CH_3}$	$C_6H_5.CO_2H$	$CO{<}{}^{C_6H_5}_{C_6H_5}$
Acetic Acid	Acetone	Benzoic Acid	Benzophenone.

This analogy is shown in the various methods of formation.

Methods of Formation.—(1) By oxidizing (a) the benzyl benzenes and (b) the benzhydrols with chromic acid:

$$CH_2{<}{}^{C_6H_5}_{C_6H_5} \xrightarrow{2O} CO{<}{}^{C_6H_5}_{C_6H_5} \xleftarrow{O} HOCH{<}{}^{C_6H_5}_{C_6H_5}.$$

If the CH_2-group contains alkyls or carboxyl, these groups will be split off by the oxidation, with the production of ketones. If the benzene residues contain alkyl groups these are converted into carboxyl groups.

(2) By the action of hot water upon the ketone chlorides (see benzophenone chloride, below).

Nucleus Syntheses.—(3) By the distillation of the calcium salts of mononucleus, aromatic monocarboxylic acids, the CO_2H-groups of which are in direct union with the benzene residue:

$$\begin{matrix} C_6H_5 . COO \\ C_6H_5 . COO \end{matrix} > Ca \longrightarrow \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} > CO + CO_3Ca.$$

(4) By the condensation of benzoic acid or its anhydride on heating with benzene and P_2O_5.

(5) By the action of benzoyl chloride on benzene, in the presence of aluminium chloride.

Phosgene reacts in the same manner, and acid chlorides are the first products. These then change into ketones (B. 10, 1854):

$$COCl_2 + C_6H_6 \xrightarrow[(Al_2Cl_6)]{-HCl} C_6H_5.COCl + C_6H_6 \xrightarrow[(Al_2Cl_6)]{-HCl} C_6H_5COC_6H_5.$$

(6) By the action of mercury diphenyl upon the acid chlorides—*e. g.*, benzoyl chloride.

Behavior.—(1) On heating with zinc-dust or hydriodic acid and amorphous phosphorus, the ketones sustain a reduction of the CO group and revert to the hydrocarbons; for example, diphenyl ketone yields diphenyl methane. (2) Sodium amalgam changes them to secondary alcohols (benzhydrols) and pinacones.

Benzophenone, Diphenyl Ketone, $CO(C_6H_5)_2$, is known in two modifications, the unstable (labile), melting at 26°, and produced on boiling the stable form, melting at 46°. The unstable modification slowly reverts to the more stable variety. This takes place rapidly, and with a very perceptible evolution of heat, upon touching it with a trace of the stable variety (B. **26**, R. 380). Benzophenone has an aromatic odor. It boils at 307° (760 mm.) and at 162° (12 mm.). It is produced according to the general methods: (1) by oxidizing diphenyl methane, unsymmetrical diphenyl ethane (p. 368), benzhydrol, diphenylacetic acid (p. 368), etc.; (2) from benzophenone chloride; (3) by the distillation of calcium benzoate; (4) by the action of P_2O_5 upon benzoic acid and benzene; (5) from phosgene or benzoyl chloride, benzene and aluminium chloride, and (6) from benzoyl chloride and mercury diphenyl. When fused with caustic potash it breaks down into benzoic acid and benzene. It is converted into diphenylmethane, benzhydrol, and benzpinacone by reduction (p. 378).

Benzophenone Homologues.—o-**Phenyltolyl Ketone**, boiling at 315°, when conducted over heated lead oxide, passes into anthraquinone (see this), while it yields anthracene when heated with zinc-dust (B. **6**, 754). m-**Phenyltolyl Ketone** boils at 314°.

p-**Tolylphenyl Ketone** is known in two modifications: the unstable (labile) *form* melts at 55°; it is hexagonal. The stable *form*, melting at 59°, is monoclinic (A. **189**, 84; B. **12**, 2299).

p-**Ditolyl Ketone** melts at 92° and boils at 333°. **Benzoyl Xylene** melts at 36° and boils at 317° (B. **17**, 2847). **Benzoyl Mesitylene** melts at 36° and boils at 317° (J. pr. Ch. [2], **35**, 486), etc. All these are most conveniently prepared by method 5.

Derivatives of Benzophenone Obtained by the Replacement of Oxygen.—**Benzophenone Chloride,** *Diphenyldichlormethane*, $CCl_2(C_6H_5)_2$, boiling at 193° (30 mm.),

is produced when PCl_5 acts upon benzophenone. When heated with water it reverts to benzophenone, while with silver it yields tetraphenylethylene (p. 378), and with zinc-dust tetraphenylethylene, α- and β-benzpinacoline (B. **29**, 1790). **Benzophenone Bromide,** $CBr_2(C_6H_5)_2$, is produced on dropping bromine into diphenylmethane heated to 150°.

Acetals of benzophenone are obtained from benzophenone chloride with sodium alcoholates, as well as from benzophenone and otho-formic ethers (see p. 189). **Dimethoxy- and diethoxydiphenyl methane** melt at 107° and 52°, and boil at 289° and 295° (B. **29**, 2932; R. 774).

Thiobenzophenone, $CS(C_6H_5)_2$, is derived from benzene by means of thiophosgene, CS_2Cl_2, and aluminium chloride. In this reaction the phenol ethers react more readily than the hydrocarbons (B. **28**, 2869). Thiobenzophenone is further produced by the action of phosphorus sulphide upon benzophenone, but best of all when an alcoholic solution of potassium sulphide reacts with benzophenone chloride. It is an intensely blue-colored oil, which congeals at lower temperatures to blue needles, and under a pressure of 14 mm. distils at 174°. The thiobenzophenones, when acted upon with metallic copper, yield tetraphenylethylene and its substitution products (B. **29**, 2944).

Diphenyldinitromethane, $(C_6H_5)_2C(N_2O_4)$, melting at 78°, results upon saturating a solution of benzophenone-oxime in ether with nitrogen tetroxide. It is changed back to benzophenone-oxime with zinc-dust and glacial acetic acid. Benzhydrylamine is also formed (B. **23**, 3490).

Imidobenzophenone, $(C_6H_5)_2C = NH$, is a colorless oil, obtained in the action of dry ammonia upon a chloroform solution of *amido-benzophenone chlorhydrate*. The chlorhydrate results when benzophenone chloride is heated with urethane to 130°. Cold water readily decomposes it into benzophenone and ammonium chloride. **Phenylbenzalsultime,** $C_6H_4\left\langle\begin{matrix} C(C_6H_5) \\ SO_2 \end{matrix}\right\rangle N$, melting at 164°, should be viewed as a derivative of imidobenzophenone, produced in the condensation of pseudosaccharin chloride (p. 216) with benzene and aluminium chloride (B. **29**, 2296).

Phenylimidobenzophenone, *Diphenylmethylene Aniline*, $(C_6H_5)_2C = N.C_6H_5$, melting at 109°, is formed from benzophenone chloride and aniline (A. **187**, 199).

Benzophenonoxime, $(C_6H_5)_2C : N.OH$, melting at 140°, is known in only one modification (for the possible existence of an unstable (*labile*) form consult B. **28**, R. 1008), while unsymmetrical benzophenones—*e. g.*, brombenzophenone and phenylethyl ketone—each form two oximes (B. **23**, 2776). It is also formed in the interaction of thiobenzophenone and hydroxylamine.

Benzophenoxime, when digested at 100° with sulphuric acid, with hydrochloric acid and glacial acetic acid, etc., sustains a peculiar molecular rearrangement into benzanilide. The isomeric benzanilide imide-chloride is produced in like manner from the imide chloride formed by PCl_5 (p. 199) (B. **22**, R. 591). The *phenylhydrazone*, $(C_6H_5)_2C : N_2H.C_6H_5$, melts at 137° (B. **19**, R. 302).

Benzophenone Halogen Derivatives are mostly produced by method 5 (p. 345). **o-Brombenzophenone,** melting at 42°, is noteworthy because of the mobility of its bromine atom. If **o-brombenzophenone oxime,** melting at 132°, be acted upon with caustic alkali it splits off hydrogen bromide and becomes *phenylindoxazene*,

$C_6H_4\left\langle\begin{matrix} C(C_6H_5) \\ O \end{matrix}\right\rangle N$ (see this) (B. **27**, 1452), while m- and p-brombenzophenone, on the other hand, yield with o-brombenzophenone two isomeric oximes (B. **25**, 3293; A. **264**, 152, 171).

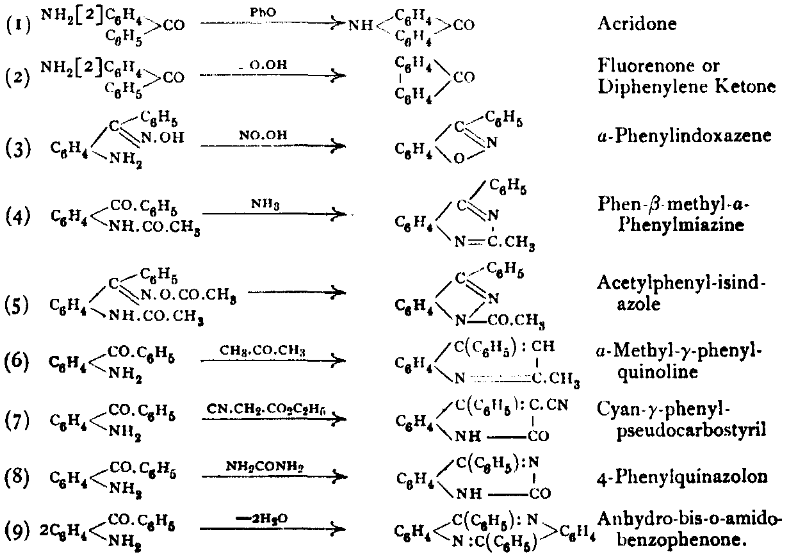
The sym. m-, p-**Dibrombenzophenones,** $(BrC_6H_4)_2CO$, melting at 142° and 171°, yield but *one oxime* (A. **264**, 160). **o,p-Dibrombenzophenone,** melting at 52°, yields *one oxime*, melting at 141°; this can be readily rearranged to p-bromphenylindoxazene (B. **27**, 1453).

o-Chlorbenzophenone Oxime shows less readily and **o-iodbenzophenone oxime** more readily than o-*brombenzophenone oxime* the formation of phenylindoxazene (B. **26**, 1250).

Nitrobenzophenones.—o-, m-, and p-**Nitrobenzophenone** melt at 195°, 94°, and 138° (B. **16**, 2717; **18**, 2401). Phenylindoxazene is produced when the oxime of the o-body is boiled with caustic soda (B. **26**, 1250). o_2-, m_2-, p_2-**Dinitrobenzophenone** melt at 188° (γ), 148° (β), and 189° (α). o,m-, o,p-, m,p-**Dinitrobenzophenone**, $(NO_2C_6H_4)_2CO$, melt at 126° (ε), 196° (δ), and 172°. o_2- and o,m-Dinitrobenzophenones are formed in the nitration of benzophenone (A. **283**, 164; B. **27**, 2111). o_2,p_2-**Tetranitrobenzophenone** melts at 225° (B. **27**, 2318). Other substituted benzophenones are described in the A. **286**, 306, etc.

Amidobenzophenones are obtained from nitrobenzophenones, from benzoic acid, dimethyl aniline and P_2O_5, benzoyl chloride, phthalanil and $ZnCl_2$ (B. **14**, 1838), etc. o-, m-, p-**Amidobenzophenone** melt at 106°, 87°, and 124°. o-Amidobenzophenone is made from the amide of o-benzoyl benzoic acid by the action of sodium hypobromite (B. **27**, 3483; A. **291**, 8). o-**Amidobenzophenone Oxime**, melting at 156°, is rearranged at high temperatures by hydrochloric acid into phenyl benzimide azole or o-phenylenebenzamidine (B. **24**, 2385). **Acetyl o-amidobenzophenone** melts at 89°. p-**Dimethylamidobenzophenone**, p-**Benzoyldimethyl Aniline**, melting at 90°, is also formed on heating *malachite green* with concentrated hydrochloric acid at 180° (A. **217**, 257; B. **21**, 3293).

Ring-formations of o-Amidobenzophenone.—(1) *Acridone* is produced when o-amidobenzophenone is heated with lead oxide (B. **27**, 3484). (2) Nitrous acid converts this o-body into *fluorenone* or *diphenylene ketone* (B. **27**, 3484). (3) *α-Phenylindoxazene* is readily obtained from o-amidobenzophenone and nitrous acid (B. **26**, 1667). (4) When acetyl-o-amidobenzophenone is heated with alcoholic ammonia it condenses to phen-β-methyl-α-phenylmiazine or α-phenyl-β-methyl quinazoline (B. **25**, 3082). (5) *Acetylphenylisindazole* (B. **24**, 2383; **29**, 1255) results when acetyl-o-amidobenzophenone oxime is rearranged by contact with Beckmann's mixture. (6) o-Amidobenzophenone condenses with acetone and sodium hydroxide to *α* methyl-3-phenylquinoline (B. **18**, 2405). (7) When heated to 200° with cyanacetic ester the product is β-cyan-γ-phenyl-pseudocarbostyril (B. **27**, R. 589). (8) With urea it yields 4-*phenylquinazolon* (B. **29**, 1310). (9) When the hydrochloride of o-amidobenzophenone is heated water is eliminated and there results an *anhydro-bis*-o-*amidobenzophenone*, which probably contains an "8-membered" ring (B. **29**, 1272):



Diamidobenzophenones.—o_2-, m_2-, p_2-**Diamidobenzophenones** melt at 134°, 173°, and 239°. Nitrous acid converts the o-body into xanthone (see this) and o-oxyfluorenone (B. **28**, 111). p_2-Diamidobenzophenone yields substantive cotton dyes (B. **22**, 988).

Tetramethyl-p_2-diamidobenzophenone, $CO<\begin{smallmatrix}C_6H_4 . N(CH_3)_2 \\ C_6H_4 . N(CH_3)_2\end{smallmatrix}$, results upon heating hexamethyl violet with hydrochloric acid (B. **19**, 109). It is technically prepared by the action of $COCl_2$ upon dimethyl aniline in the presence of $AlCl_3$. It melts at 173°. Nitrous acid converts it into nitrosotrimethyldiamidobenzophenone (B. **24**, 3198). Dimethylaniline and PCl_3 convert it into methyl violet, while it yields *Victoria blue* with phenylnaphthylamine. Its *oxime* melts at 233° (B. **19**, 1852). Its *hydrazone* melts at 174° (B. **20**, 1112).

Tetramethyl-p_2-diamido-thiobenzophenone, $CS[C_6H_4 . N(CH_3)_2]_2$, results from the action of hydrogen sulphide upon an alcoholic auramine solution heated to 60°, or it can be prepared from dimethylaniline and $CSCl_2$. It consists of ruby red crystalline leaflets with a blue lustre or a cantharides-green crystalline powder, melting at 202° (B. **20**, 3266, 3290).

Auramine, *Tetramethyl-p_2-diamido-imidobenzophenone Hydrochloride,*

$$[(CH_3)_2NC_6H_4]_2C = NH . HCl, \quad \text{or} \quad \begin{smallmatrix}Cl(CH_3)_2N = C_6H_4 \\ (CH_3)_2N - C_6H_4\end{smallmatrix}\!\!>C . NH_2 \quad (B. \mathbf{26}, R. 406),$$

results when tetramethyldiamidobenzophenone is heated with ammonium chloride and zinc chloride, as well as from p-dimethylamidobenzamide by the action of dimethylaniline and zinc chloride (B. **28**, R. 86). Perfectly analagous dyestuffs are obtained from the primary anilines and diamines (B. **20**, 2844; **28**, R. 65). **Auramine,** golden-yellow leaflets, is important as a cotton dye. Cotton mordanted with tannin is colored a beautiful yellow by this salt.

Potassium cyanide changes it to the nitrile of the corresponding tetramethyldiamidodiphenylacetic acid (B. **27**, 3294).

(ϵ)o,m-, (δ)o,p-, (ζ)m,p-**Diamidobenzophenones** melt at 80°, 128°, and 126° (A. **283**, 149; B. **28**, 111).

Oxybenzophenones are formed: (1) From amidobenzophenones; in this change the o-amidobenzophenones (p. 347) pass chiefly into fluorenones. (2) By decomposing the xanthones, which may be viewed as cyclic phenyl ethers of o_2-dioxybenzophenones, with caustic potash. (3) By the condensation of benzoic acids or oxybenzoic acids and phenols with zinc chloride or phosphorus oxychloride (B. **26**, R. 587), sulphuric acid or tin tetrachloride (B. **23**, R. 43, 188; **24**, 967). (4) From phenols by means of benzoyl chloride, zinc-dust, or zinc chloride, or aluminium chloride (B. **12**, 261). (5) By the action of benzotrichloride and zinc oxide (B. **10**, 1969) upon phenols or their benzoyl esters. (6) By the action of alkalies upon benzotrichloride and phenols (B. **24**, 3677).

Oxybenzophenones containing but one hydroxyl-group in one benzene residue.—o-**Oxybenzophenone,** o-*Benzoylphenol,* melting at 41°, is produced, together with the phenyl ester of benzoic acid, by the 6th method of formation; also from phenylindoxazone (see this) upon heating it with hydriodic acid and phosphorus (B. **29**, R. 350). The best method, however, consists in treating methyl salicylic chloride with benzene and aluminium chloride (B. **29**, 824). m-**Oxybenzophenone,** melting at 116°, is produced according to method 1 (B. **24**, 4044). p-**Oxybenzophenone,** melting at 134°, is produced by methods 1, 4, and 5 (B. **25**, 3533). (γ)o_2-, (β)m_2-, (α)p_2-**Dioxybenzophenones** *melt at 173°, 162°, and 210°*, and (ϵ)o,m-, (δ)o,p-**Dioxybenzophenones** melt at 126° and 142°. They are obtained from the corresponding diamidobenzophenones.

o_2-Dioxybenzophenone is also made from its anhydride, xanthone or diphenylene ketone oxide, by careful fusion with potassium hydrate (B. **19**, 2609). o,p- and p_2-Dioxybenzophenones are also produced in the condensation of salicylic acid and phenol with tin tetrachloride (A. **283**, 175). p_2-Dioxybenzophenone appears also in the decomposition of aurine, benzaurine, phenolphthaleïn, and rosaniline upon heating them with water or caustic potash (B. **16**, 1931).

Oxybenzophenones containing more than one hydroxyl attached to one Benzene-nucleus.—These are prepared mainly by method 3 (p. 345). Mention must be made of the ketones obtained from pyrogallic acid and gallic acid, for they, like alizarine, are dyes.

The dyestuff prepared from benzoic acid and pyrogallol melts at 140°. It bears the name *alizarine yellow* A in trade (A. **269**, 295).

Benzoyl-2,5-dioxybenzene, $C_6H_5COC_6H_3[2,5](OH)_2$, melting at 125°, is obtained from benzaldehyde and quinone, exposed to sunlight (B. **24**, 1340; p. 167).

The barks of coto and paracoto, found in Bolivia, and possessing therapeutic value, contain a series of benzophenone derivatives. They are:

Cotoïn, $C_6H_5 . CO . C_6H_2(OH)_2(OCH_3)$, melting at 130°;

Hydrocotoïn, $C_6H_5 . CO . C_6H_2(OH)(OCH_3)_2$, melting at 98°;

Methyl Hydrocotoïn, $C_6H_5 . CO . C_6H_2(OCH_3)_3$, melting at 113° (B. **25**, 1119; **26**, 2340; **27**, 419), which are methyl ethers of benzoyl phloroglucin; and **Protocotoïn,** $(CH_3O)_2(HO) . C_6H_2 . CO . C_6H_3(O_2CH_2)$, melting at 141°, as well as **Methyl Protocotoïn,** $(CH_3O)_3 . C_6H_2 . CO . C_6H_3(O_2CH_2)$, melting at 134°, derivatives of 1,3,5-trioxybenzoprotocatechone.

4. CARBOXYLIC ACIDS OF THE DIPHENYLMETHANE GROUP.

There are three classes of these acids: A. *Diphenylmethane Carboxylic Acids;* B. *Benzhydrol Carboxylic Acids;* C. *Benzophenone Carboxylic Acids.*

A. *Diphenylmethane Carboxylic Acids.*—o-, m-, p-**Benzyl-benzoic Acids,** $C_6H_5 . CH_2 . C_6H_4 . CO_2H$, melt at 117°, 107°, and 154°. When the *o-acid* is digested with sulphuric acid, *anthranol* (see this) is produced (B. **25**, 3022; **27**, 2789; A. **291**, 17) (B. **9**, 633). **o-Cyandiphenyl Methane,** melting at 19° and boiling at 313°, is obtained from o-cyanbenzyl chloride by means of benzene and aluminium chloride, as well as from o-amidodiphenylmethane.

Benzyliso- and -terephthalic Acid, $C_6H_5 . CH_2 . C_6H_3(CO_2H)$—see B. **9**, 1765.

Diphenylmethane-o$_2$-dicarboxylic Acid, $CH_2(C_6H_4[2]CO_2H)_2$, melting at 254°, results from the reduction of the lactone of benzhydrol-o$_2$-dicarboxylic acid, and that of the dilactone of benzophenone-o$_2$-dicarboxylic acid. Concentrated sulphuric acid changes it to anthranolcarboxylic acid (A. **242**, 253).

Diphenylmethane-m$_2$-dicarboxylic Acid melts at 220–225°. **Diphenylmethane-p-dicarboxylic Acid** melts at 290° (B. **27**, 2324).

B. *Benzhydrol Carboxylic Acids.*—o-**Benzhydrylbenzoic Acid Lactone,** *Phenylphthalide,* $C_6H_4\left\{\begin{array}{l}[1]CH - C_6H_5 \\ \quad\diagdown \\ [2]COO\end{array}\right.$, melting at 115°, is formed by the reduction of o-benzoyl benzoic acid, and by the breaking down of benzhydrol-o$_2$-carboxylic acid on the application of heat. The acid corresponding to the lactone is not capable of existing as such; its salts, however, are known. PCl_5 converts the lactone into anthraquinone (B. **21**, 2005). **o-Cyanbenzhydrol,** $C_6H_5(CHOH)C_6H_4[2]CN$, has been prepared from o-*cyandiphenylchlormethane,* $C_6H_5CHCl . C_6H_4CN$, the reaction product from chlorine and cyandiphenylmethane (B. **29**, 1315). m- and p-**Benzhydrylbenzoic Acid** melt at 121° and at 164° (A. **220**, 242). p-**Tolylphthalide** melts at 129°; for its homologues see A. **234**, 237. **Oxyphenylphthalide,** $C_6H_4\left\{\begin{array}{l}CH . C_6H_4 . OH \\ \quad\diagdown \\ COO\end{array}\right.$, melting at 180°, is obtained from phthalaldehydic acid (p. 236), phenol, and sulphuric acid (73 per cent.) (B. **27**, 2632).

Benzhydrol-o$_2$-lactone Carboxylic Acid, $C_6H_4\left\{\begin{array}{l}CH—C_6H_4CO_2H \\ \quad\diagdown \\ COO\end{array}\right.$, melting at 202°, is produced on heating benzhydroltricarboxylic acid mono-lactone, $C_6H_4\begin{array}{l}\diagup C\begin{array}{l}<CO_2H \\ \diagdown C_6H_4.CO_2H\end{array} \\ \diagdown COO\end{array}$, the reaction-product of alkalies upon diphthalic acid (A. **242**, 233).

C. *Benzophenone Carboxylic Acids* are formed (1) in the oxidation of the alkyl-diphenylmethanes, alkylbenzophenones, diphenylmethane carboxylic acids, and benzhydrol carboxylic acids; (2) from benzoyl chloride and benzoic anhydride with zinc

chloride (B. **14**, 647); (3) from phthalic anhydride and benzene with aluminium chloride.

o-Benzoyl Benzoic Acid, $C_6H_5.CO.C_6H_4[2]CO_2H + H_2O$, melts when anhydrous at 127°. It is produced by oxidizing o-tolylphenylmethane, o-methylbenzophenone, o-benzyl- and o-benzhydrylbenzoic acid. It can be prepared by method 3. Heated with phosphorus pentoxide, water is eliminated and anthraquinone is produced. Anthracene is produced when it is heated with zinc-dust. With benzene and aluminium chloride orthobenzoyl-benzoic acid yields phthalophenone; with phenol and stannic chloride, oxyphthalophenone. When digested with acetic anhydride (B. **14**, 1865) it changes to—

Aceto-benzoyl Benzoic Acid, $C_6H_4\begin{cases}[1]C\begin{matrix}\diagup C_6H_5 \\ -O.CO.CH_3 \\ \diagdown \end{matrix} \\ [2]COO\end{cases}$, melting at 117° (compare aceto-lævulinic acid). The *oxime anhydride* melts at 162°. It is formed when hydroxylamine hydrochloride acts upon benzoyl benzoic acid. At 130° it yields phthalanil (B. **26**, 1262, 1795). *Phenyllactazam*, $C_6H_4\begin{cases}[1]C(C_6H_5):N \\ [2]CO \;—\; N.C_6H_5\end{cases}$, melting at 181° (compare lævulinic acid) (B. **18**, 805).

Chlorinated *benzoyl benzoic acids* have been prepared from chlorinated phthalic anhydrides by the action of benzene and aluminium chloride (A. **238**, 338), and homologous *methyl benzoyl benzoic acids* from phthalic anhydride and toluene or other methyl benzenes (B. **19**, R. 686).

m-Benzoyl Benzoic Acid, $C_6H_5.CO.C_6H_4[3]CO_2H$, melting at 161°, is made from isophthalic chloride, benzene, and aluminium chloride (A. **220**, 236; B. **13**, 320). **p-Benzoyl Benzoic Acid**, melting at 194°, is prepared according to method 1 (B. **9**, 92).

Benzophenone-o$_2$-dicarboxylic Acid, $CO(C_6H_4[2]CO_2H)_2$, melts irregularly at 150–200° with the elimination of water and a change to the dilactone. It is produced by oxidizing benzhydrol-o$_2$-lactone carboxylic acid with potassium permanganate. *Benzophenone-dicarboxylic Dilactone*, $\begin{matrix}COO & \diagdown & & \diagup & OCO \\ | & & C & & | \\ C_6H_4 & \diagup & & \diagdown & C_6H_4\end{matrix}$, melting at 212°, is produced on boiling the aqueous solution of the acid, as well as by digesting its alcoholic solution with hydrochloric acid (A. **242**, 246).

Benzoyl Phthalic Acid, $C_6H_5CO.C_6H_3[2,3](COOH)_2$, from hemimellitic anhydride, benzene and Al_2Cl_6, melts at 183° with the formation of an anhydride (A. **290**, 217). Concentrated sulphuric acid converts it into anthraquinone carboxylic acid.

Benzyl Diphenyls, $C_6H_5.CH_2.C_6H_4.C_6H_5$, are formed from diphenyl, benzyl chloride, and zinc-dust. **p-Benzyl Diphenyl** melts at 85° and boils at 285° (100 mm.). **Isobenzyl Diphenyl** melts at 54° and boils at 283–287° (110 mm.) (B. **14**, 2242).

p-Phenylbenzyl-o-benzoic Acid, $C_6H_5[4]C_6H_4[1]CH_2[2]C_6H_4[1]CO_2H$, melts at 184°, and **p-Phenylbenzhydryl-o-benzoic Acid**, $C_6H_5[4]C_6H_4[1]CH(OH).C_6H_4[2]CO_2H$, melts at 204°. Both are produced in the reduction of **p-Phenylbenzoyl-o-benzoic Acid**, $C_6H_5[4]C_6H_4[1]CO[2]C_6H_4[1]CO_2H$, melting at 225°, which results from the action of aluminium chloride upon a ligroïne solution of diphenyl and phthalic anhydride (A. **257**, 96; J. pr. Ch. [2], **41**, 149).

Dibenzyl Benzenes.—The second benzyl residue can be introduced into benzene and its homologues, containing replaceable hydrogen atoms attached to the nucleus, by the same reactions which were employed in introducing the first benzyl residue—*i. e.*, by the action of zinc-dust (B. **9**, 31) or aluminium chloride upon a solution of the benzyl chloride in the hydrocarbons, and by the action of sulphuric acid upon benzene and methylal (B. **6**, 221). α- and **β-Dibenzylbenzene** melt at 86° and 78°.

Dibenzoylbenzenes, $C_6H_4<\begin{matrix}CO.C_6H_5 \\ CO.C_6H_5\end{matrix}$, **phthalophenones**, phenylene diphenyl ketones. The ortho and para derivatives are produced by the oxidation of the corresponding dibenzylbenzenes (B. **9**, 31).

The *meta* and *para* compounds may be obtained from meta- and para-phthalyl chlo-

rides with benzene and $AlCl_3$ (B. **13**, 320), whereas the so-called orthophthalyl chloride yields diphenylphthalide.

Orthophthalophenone melts at 146°; **meta- or isophthalophenone** at 100°; **terephthalophenone** at 160° (B. **19**, 146, 154).

III. TRIPHENYLMETHANE GROUP.

Triphenylmethane, tolyldiphenylmethane, and ditolylphenylmethane are the parent hydrocarbons from which originate the *rosaniline dyes*, the *malachite-greens*, the *aurines*, and *phthaleïns*, from which they can be obtained by various transposition and decomposition reactions. However, in no one of these instances do they constitute the starting-out material for the technical preparation of the mentioned dyes.

1. **Hydrocarbons.**—The methods of forming the triphenylmethane hydrocarbons are evident if one simply makes more general those methods which are employed in the preparation of triphenylmethane.

Triphenyl Methane, $CH(C_6H_5)_3$, melts at 92° and boils at 358°. It is produced (1) by the action of benzal chloride upon mercury diphenyl (1872, Kekulé and Franchimont, B. **5**, 907); (2) from benzal chloride or benzotrichloride and benzene (a) by the action of zinc-dust, (b) with aluminium chloride (B. **12**, 976, 1468; **14**, 1526).

(3) From chloroform or carbon tetrachloride and benzene aided by $AlCl_3$ (A. **194**, 254; **227**, 107; B. **18**, R. 327).

(4) By the action of P_2O_5 at 140° (B. **7**, 1204) upon benzhydrol and benzene.

(5) By the action of nitrous acid and alcohol upon di- and triamidotriphenyl methane sulphate (A. **206**, 152).

The latter reaction is of the greatest fundamental importance in demonstrating the connection between p-rosaniline and triphenylmethane.

Triphenylmethane crystallized from benzene contains *benzene of crystallization*, $CH(C_6H_5)_3 + C_6H_6$, melting at 75°, and from thiophene it separates with *thiophene of crystallization*, $CH(C_6H_5)_3 + C_4H_4S$ (B. **26**, 853). It is oxidized to triphenyl carbinol, and is reduced by hydriodic acid and some red phosphorus at 280° to benzene and toluene. When heated with potassium it yields *triphenyl methane potassium* $(C_6H_5)_3CK$, which combines with CO_2 to potassium triphenyl acetate (p. 369).

o-, m-, p-**Methyl Triphenyl Methane,** *diphenyl*-o-, m-, p-*tolyl methane*, $(C_6H_5)_2$-$CH.C_6H_4.CH_3$, melt at 59°, 62°, and 71°. The o-compound was obtained by the action of nitrous acid and alcohol upon leucaniline sulphate (A. **194**, 282).

Diphenyl-o-, m-, p-xylylmethanes melt at 68°, 61°, and 92°; they have been obtained from benzhydrols with o-, m-, and p-xylene by means of P_2O_5 (B. **16**, 2360).

Nitrosubstitution Products.—m- and p-**Nitrotriphenyl Methane,** $NO_2.C_6H_4.CH$-$(C_6H_5)_2$, melting at 90° and 93°, are obtained from m- and p-nitrobenzaldehyde, benzene, and zinc chloride (B. **21**, 188; **23**, 1622).

When triphenyl methane is dissolved in fuming nitric acid (sp. gr. 1.5) it forms **p-trinitro-phenyl methane,** $CH(C_6H_4[4]NO_2)_3$, which melts at 206°. Sodium alcoholate converts the nitro-compound into a deep violet-colored sodium salt. It dissolves in alcoholic potassium hydroxide with a violet color (B. **21**, 2476).

p-Trinitro-diphenyl-m-tolyl Methane, $(NO_2[4]C_6H_4)_2CH.C_6H_3[4]NO_2[3]CH_3$.

Amido-derivatives are produced (1) by the reduction of the corresponding nitro-bodies; (2) by reduction of the corresponding amido-carbinols, the color bases of the

malachite-green and rosaniline groups, as the *leuco-derivatives* of which they are frequently designated; (3) by the condensation of benzhydrol or benzaldehyde and aniline hydrochloride, or dimethyl aniline hydrochloride with P_2O_5 or $ZnCl_2$. When oxidized with chloranil, or PbO_2 and hydrochloric acid, etc., their salts change to those of the color-bases to which malachite-green and rosaniline belong; they are derived from triphenyl carbinol.

m-**Amidotriphenyl Methane**, $(C_6H_5)_2CHC_6H_4[3]NH_2$, melting at 120°, is obtained from m-nitrotriphenylmethane (B. **21**, 189).

p-**Amidotriphenyl Methane**, melting at 84°, is formed (1) from p-nitrotriphenyl methane (B. **23**, 1023), and (2) from benzhydrol, aniline hydrochloride, and zinc chloride (A. **206**, 155).

p-**Dimethylamidotriphenyl Methane**, $(C_6H_5)_2CH.C_6H_4[4]N(CH_3)_2$, melting at 132°, is formed from benzophenone chloride and dimethyl aniline, as well as from benzhydrol and dimethyl aniline with P_2O_5 (A. **206**, 113), as well as from benzophenone, dimethyl aniline, and zinc chloride (A. **242**, 341). p-**Acetamidotriphenyl Methane** melts at 176° (B. **24**, 728).

p_2-**Diamido-triphenyl Methane**, $C_6H_5.CH(C_6H_4[4]NH_2)_2$, melting at 139°, + C_6H_6 at 106°, the parent substance of *malachite-green*, is obtained (1) from benzal chloride and aniline with zinc-dust; (2) from benzaldehyde with aniline hydrochloride on heating with zinc chloride to 120° (B. **15**, 676), or by boiling benzaldehyde with aniline and hydrochloric acid (B. **18**, R. 334); (3) by reducing diamidotriphenyl carbinol chloride with zinc-dust.

p_2-**Tetramethyl-diamido-triphenyl Methane**, $C_6H_5.CH[C_6H_4-[4]N(CH_3)_2]_2$, *leucomalachite-green*, is dimorphous, and crystallizes in leaflets, melting at 93–94°, or in needles, which melt at 102°. The first modification is obtained pure by crystallization from alcohol, the second from benzene. It is obtained by methylating p_2-diamido-triphenylmethane, as well as by the action of benzaldehyde upon dimethyl aniline. Technically, it is made by the condensation of benzaldehyde and dimethyl aniline with hydrochloric or sulphuric acid (formerly zinc chloride or oxalic acid). By oxidation it becomes p_2-tetramethyldiamido-triphenyl carbinol, the basis of malachite-green.

o- and m-**Nitro-p_2-diamido-triphenyl Methane** are produced in the condensation of o- and m-nitrobenzaldehyde with aniline sulphate by means of zinc chloride. The m-body melts at 136° (B. **13**, 671; **16**, 1305).

p-**Nitro-p_2-diamido-triphenyl Methane** is obtained from p-nitrobenzaldehyde, just as the o- and m-compounds are prepared. See p-leucaniline (B. **25**, 676).

Benzaldehyde and the nitrobenzaldehydes condense with o- and p-toluidine, just as they do with aniline and dimethyl aniline (B. **18**, 2094), whereas m-toluidine and m-derivatives of aniline only react readily if the amido-group is methylated (B. **20**, 1563).

Triamidotriphenyl Methanes result from the reduction of the nitro- and nitroamidotriphenyl methanes and of the triamidotriphenyl carbinols. The latter are the rosaniline bases if the three amido-groups occur in the p-position with reference to the C(OH) group. Their reduction products are also called leucanilines. These are white precipitates, and when oxidized yield the carbinols:

o,p_2-Triamidotriphenyl Methane, or o-*Leucaniline*,
and m,p_2-Triamidotriphenyl Methane, or *Pseudoleucaniline*,
and p_3-Triamidotriphenyl Methane, or *Paraleucaniline*,

which, upon oxidation, yield dyestuffs. That from the o-body is brown in color, that from the m-body is violet, while that from the p-compound

is *pararosaniline* (p. 356). p-Triamidotriphenylmethane is also produced in the condensation of p-amidobenzaldehyde and aniline with zinc chloride; its tridiazochloride, $CH(C_6H_4 . N_2Cl)_3$, when boiled with alcohol, forms triphenylmethane.

p_3-**Triamido-diphenyl-m-tolyl Methane, Leucaniline,** $(NH_2[4]-C_6H_4)_2CH . C_6H_3[4](CH_3) . NH_2[3]$, is the leuco-compound corresponding to the chief constituent of rosaniline obtained by the reduction of trinitro-diphenyl meta-tolyl methane, and is also made by digesting the fuchsine salts with ammonium sulphide, or zinc-dust and hydrochloric acid. By diazotizing and replacing the diazo-groups by hydrogen (best by dissolving in concentrated sulphuric acid, conducting nitrous acid into the same, and boiling with alcohol) leucaniline is changed into diphenyl-m-tolyl methane.

2. **Carbinols** are formed by oxidizing the triphenyl methane hydrocarbons, their nitro- and amido-compounds.

Triphenyl Carbinol, $(C_6H_5)_3C . OH$, melting at 159°, boils without decomposition above 360°, and is produced by oxidizing triphenylmethane with chromic acid in glacial acetic acid (B. **14**, 1944), on boiling triphenyl-brom-methane or triphenylchlormethane with water (B. **7**, 1206), or with a soda solution, as well as from pararosaniline (B. **26**, 2125), and from oxalic ester, or benzaldehyde, or benzophenone with sodium and brombenzene in ether (B. **28**, 2514). The *methyl ether* melts at 82°, and the *acetate* at 99° (A. **227**, 116).

Diphenyl-m-tolyl-carbinol, $(C_6H_5)_2 . C(OH) . C_6H_4[3]CH_3$, melting at 150°, is prepared from diphenyl-m-tolyl methane in the same manner as with triphenyl carbinol (A. **194**, 283).

Triphenylchlormethane, *Triphenyl Carbinol Chloride*, $(C_6H_5)_3CCl$, melting at 105–115°, results upon treating triphenyl carbinol with PCl_5, and by the action of aluminium chloride upon carbon tetrachloride in benzene solution. When heated above 250° it breaks down into diphenylene phenyl methane, $C_6H_5 . CH \langle {C_6H_4 \atop C_6H_4} \rangle$, and hydrochloric acid.

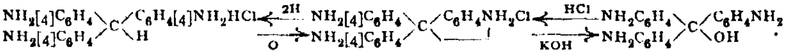
Triphenyl-brom-methane, $(C_6H_5)_3CBr$, melting at 152°, is produced when bromine acts in sunlight upon triphenylmethane dissolved in carbon disulphide (A. **227**, 110). Above 200° it breaks down like the chloride. Potassium cyanide transposes it into triphenylacetonitrile (p. 370).

Triphenyl-methylamine, *Triphenylcarbinolamine*, $(C_6H_5)_3C . NH_2$, melting at 103°, is produced on conducting dry ammonia gas into a benzene solution of triphenylcarbinol bromide or chloride (B. **17**, 442, 741). **Triphenylcarbinolphenylamine,** $(C_6H_5)_3C . NH . C_6H_5$, melts at 144° (B. **17**, 703, 746).

Diphenylbenzylsultam, $C_6H_4 \left\{ {[1]C(C_6H_5)_2 \atop [2]SO_2} \right\rangle NH_2$, melting at 210°, may be viewed as a derivative of triphenylmethylamine. It is formed, together with phenylbenzalsultime (p. 346), in the condensation of pseudosaccharin chloride with benzene and Al_2Cl_6 (B. **29**, 2296). m- and p-**Nitrotriphenyl-carbinol,** $(C_6H_5)_2C(OH)C_6H_4NO_2$, melt at 75° and at 136° (B. **21**, 190; **23**, 1623).

p_3-**Trinitrotriphenyl Carbinol,** $(NO_2[4]C_6H_4)_3 . C . OH$, melting at 171°, is prepared from p_3-trinitrotriphenyl methane by the action of chromic acid in glacial acetic acid. It yields p-rosaniline upon reduction.

Amidotriphenyl Carbinols.—p_2-Diamidotriphenyl-carbinol and p_3-triamido carbinols, of this class, deserve especial consideration. p_2-Tetramethyldiamidotriphenyl-carbinol is the basis of malachite-green and p_3-triamidotriphenyl-carbinol that of p-rosaniline. The free amido-carbinols are colorless. In contact with acids water is eliminated and color-salts result. These are also formed by the direct oxidation of the salts of the leuco-compounds, and pass into the latter upon reduction. Thus, p-leucaniline hydrochloride (1) yields, upon oxidation, p-rosaniline chloride, from which colorless p_3-triamidotriphenyl-carbinol is separated by bases; hydrochloric acid converts this compound again into p-rosaniline chloride:



The formula of p-rosaniline chloride can be more conveniently written than shown in the diagram by assuming it to be derived rather from the diketo formula than from the superoxide formula of quinone-imide (p. 172), and the valence of the nitrogen still be considered as five:

$$(NH_2[4]C_6H_4)_2C = C_6H_4[4] = NH_2Cl.$$

As the triamidotriphenyl-carbinols are considerably stronger bases than the corresponding triamidotriphenyl-methanes, and as two amido-groups behave differently than the third, the following constitutional formula has been suggested for p-triamidotriphenyl carbinol (B. **28**, 207):

$$(NH_2[4]C_6H_4)_2C.O(C_6H_4[4]NH_3).$$

m- and p-**Amidotriphenyl Carbinol,** $(C_6H_5)_2C(OH)C_6H_4NH_2$, melt at 155° and 116° (B. **21**, 190; **23**, 1625). The salts of these carbinols do not possess color-power.

p_2-Diamidotriphenyl Carbinol.—The chloride of this dye, soluble with a reddish-violet color, is produced on heating aniline hydrochloride, nitrobenzene, and benzotrichloride with iron filings (A. **217**, 242).

p_2-Tetramethyl-diamido-triphenyl Carbinol, $C_6H_5.C(OH)[C_6H_4[4]N(CH_3)_2]_2$, melting at 132°, crystallizes from benzene in colorless forms. It is obtained from its salts (malachite-green) by precipitation with the alkalies and by oxidizing an alcoholic solution of p_2-tetramethyl-diamido-triphenylmethane with chloranil (A. **206**, 130).

The free base yields almost colorless solutions with acids in the cold; upon standing, more rapidly on heating, the solution acquires a green color and then contains the green salts—*malachite-greens*—of the anhydro-base of the carbinol (B. **12**, 2348).

Malachite Green, *Bitter Almond Oil Green,* $C_6H_5.C<\begin{matrix}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2Cl\end{matrix}$,

the hydrochloride of the anhydro-base, is produced when zinc chloride acts upon a mixture of benzotrichloride and dimethylaniline, or upon a mixture of benzoyl chloride and dimethyl aniline (A. **206**, 137).

Technically, leucomalachite green is first prepared and its hydrochloride then oxidized with lead peroxide. Upon heating to 200° with concentrated hydrochloric acid it breaks down into dimethyl aniline and p-benzoyldimethyl aniline (p. 347). The *iodmethylate*, $C_6H_5C(OCH_3)[C_6H_4N(CH_3)_3I]_2 + 2H_2O$, is obtained on heating p_2-diamido-triphenyl-carbinol and p_2-tetramethyldiamido-triphenyl-carbinol with methyl iodide and methyl alcohol.

Malachite green, characterized by its strong coloring power, usually appears in trade in the form of its *zinc chloride* double salt, $(C_{23}H_{25}N_2Cl)_3 . 2ZnCl_2 + 2H_2O$, or its *oxalate*, $(C_{23}H_{25}N_2)_2 3C_2O_4H_2$.

History.—Malachite green, or *bitter almond oil green*, was obtained in 1877 by O. Fischer in the oxidation of p_2-tetramethyldiamido-triphenyl methane. He obtained the latter compound by condensing benzaldehyde with dimethylaniline. Doebner (1878) showed how malachite green could be prepared from benzotrichloride and dimethyl aniline.

Brilliant Green, *Solid Green*, *New Victoria Green*, is the tetra-ethyl derivative, corresponding to malachite green, which is made from diethylaniline and benzaldehyde (B. 14, 2521). The color is more yellow-tinted than that of malachite green.

Acid Green is a dye obtained from benzaldehyde and benzyl-ethyl aniline by condensation, oxidation, and sulphonation. The sulpho-groups are in the benzyl residue (B. 22, 588).

Nitromalachite Greens have been prepared with o-, m-, and p-nitrobenzaldehydes and dimethyl aniline as the starting-out substances (B. 15, 682).

Triamidotriphenyl Carbinols.—p_3-*Triamidotriphenyl carbinol*, p_3-*triamidodiphenyl*-m-*tolyl carbinol*, and their methyl, ethyl, benzyl, and phenyl derivatives, are of the highest importance for the coal-tar color industry. Their salts with one equivalent of acid, hydrochloric or acetic, constitute the group of rosaniline dyes in the more restricted sense. Like malachite green, the rosaniline dye-substances are free from carbinol oxygen, as the salt formation is accompanied by an intramolecular anhydride formation. The carbinols separated from these salts by alkalies are colorless, but turn red, however, on exposure to the air.

Fuchsine is the dyestuff produced in the oxidation of a mixture of aniline, o-toluidine, and p-toluidine. It is the so-called *red oil* (p. 76). **Rosaniline** is the chief ingredient of fuchsine. It is the hydrochloride or acetate of anhydro-p_3-triamidodiphenyl-m-tolyl carbinol, $C_{20}H_{19}N_3 . HCl + 4H_2O$ or $C_{20}H_{19}N_3 . C_2H_4O_2$. The monacid salts combine with two additional equivalents of acid, forming yellowish-brown colored salts, which water decomposes into the stable, *monacid* salts with intense colors. These are applied as dyes. They are mostly readily soluble in water and alcohol, and crystallize in metallic, greenish crystals. Their solutions are carmine-red in color, and stain animal tissue directly violet-red, while vegetable fiber (cotton) must first be mordanted (tannin). Fuchsine combines with sulphurous acid, forming the readily soluble, colorless *fuchsine-sulphurous acid*.

Aldehydes impart a red color to this solution, which serves as a reagent for them.

Oxidants used with *red oil* (p. 76) are stannic chloride (Verguin, 1859), mercurous and mercuric nitrates, arsenic acid at 180–200° (Medloc, Nicholson, Girard and de Laire, 1860); nitrobenzene with a little ferrous chloride or ammonium vanadate at 180–190°, when the half of the red oil is applied as hydrochloride (Coupier, 1869; compare B. 6, 25, 423, 1072).

In the *arsenic acid method* the fuchsine is obtained in the form of arsenites, which are then converted into the chlorhydrate or acetate, and obtained free from arsenious acid by recrystallization.

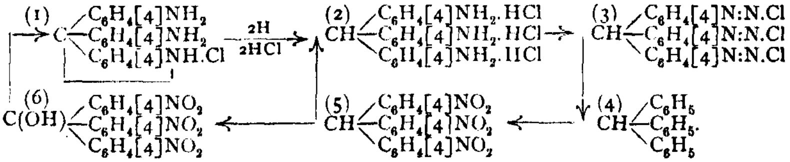
The *nitrobenzene method* yields immediately a fuchsine which is not poisonous. The nitrobenzene only acts as an oxidant, without entering into the fuchsine formation at all.

Fuchsine is not formed either from aniline or from p-toluidine, or from o-toluidine alone. Even a mixture of aniline with o-toluidine is not oxidized to fuchsine. However, not only a mixture of aniline with o- and p-toluidine yields fuchsine, but in the oxidation of a mixture of aniline and p-toluidine a dye, with the properties of fuchsine, called pararosaniline, is produced. This is also present in small amount in the fuchsine made from aniline and o- and p-toluidines; whereas the principal constituent of ordinary fuchsine consists of the next higher homologue of pararosaniline, namely, rosaniline (B. 13, 2204).

By-products in the Formation of Fuchsine.—The fuchsine melt contains, in addition to 34 per cent. of fuchsine, other violet and brown dyes: *mauvaniline*, *violaniline*, substances belonging probably to the indulines, and other less thoroughly investigated substances, as well as slight amounts of a yellow acridine dye, known as *phosphin* or *chrysanilin* (see this).

History of the Recognition of the Constitution of Rosaniline and Pararosaniline.—A. W. Hofmann was the first person to engage in a scientific study of fuchsine. He began his investigations in the sixties, and was led, as a consequence, to present a formula for fuchsine and its fundamental dye-base. He became acquainted with numerous derivatives of fuchsine, especially the methyl and ethyl violet fuchsines. He assumed that the nitrogen atoms held together the radicals in the fuchsine molecule. However, Kekulé (1867) argued for the possibility that the methyl groups of the toluidine molecules, necessary for the production of fuchsine, afforded the connection. K. Zulkowsky (1869) assumed the presence of three amido-groups in fuchsine, and considered it a derivative of a hydrocarbon with the formula $C_{18}H_{14}$. Gradually, however, the conviction grew that fuchsine sprang from a higher aromatic hydrocarbon. This idea had its basis or origin in the experiments of Wanklyn, Caro, Graebe, Dale, Schorlemmer, and others, which, in the main, established the relationship of fuchsine to rosolic acid. The "keystone to that extended series of experimental and speculative investigations" was the conversion (1878) of pararosaniline, prepared by the oxidation of aniline and p-toluidine, into triphenylmethane. This was the work of Emil and Otto Fischer. The hydrocarbon prepared by them from rosaniline, the chief constituent of fuchsine, proved to be diphenyl-m-tolylmethane.

Triphenylmethane (4) is formed in the decomposition of the tridiazosulphate of paraleucaniline with alcohol. In the diagram the formula of the tridiazochloride (3) of paraleucaniline (2) is used for the sake of simplicity. Concentrated nitric acid converts triphenylmethane into p_3-trinitrotriphenylmethane (5), which, upon reduction, yields p_3-triamidotriphenylmethane, or paraleucaniline (2). The latter, by oxidation, is converted into p_3-trinitrotriphenyl carbinol (6). On oxidizing paraleucaniline with arsenic acid, or by reducing p_3-trinitrotriphenyl carbinol with acetic acid and zinc-dust, pararosaniline (1) results. The following diagram illustrates this series of reactions, which were carried out, beginning with rosaniline itself (A. 194, 242):



Pararosaniline is produced by oxidizing a mixture of aniline and p-toluidine according to the arsenic acid or nitrobenzene method (p. 355). The reaction may be imagined to proceed in that a molecule of p-toluidine is oxidized to p-amidobenzaldehyde, the latter then condenses with two molecules of aniline to paraleucaniline or p_3-triamidotriphenylmethane (p. 355), from which, finally, pararosaniline results by oxidation.

When working with small quantities the most convenient way of oxidizing aniline and p-toluidine to pararosaniline consists in using mercuric chloride (B. **24**, 3552). An interesting formation of pararosaniline is that of heating aniline with carbon tetrachloride to 230°, when the latter furnishes the linking carbon atom. The hydroiodide of pararosaniline results by using iodoform, CHI_3.

Pararosaniline is further formed by the reduction of p_3-trinitrotriphenyl carbinol (see above); by heating p_3-nitrodiamido-triphenyl methane with ferrous chloride (B. **15**, 678); triamidotriphenyl carbinol is also formed by moderated reduction of p-nitrodiamido-triphenylmethane, inasmuch as the diamido-diphenylmethane-phenylhydroxylamine, $(C_6H_4NH_2)_2CH \cdot C_6H_4 \cdot NHOH$, formed at first, rearranges itself (B. **29**, R. 32); further, by heating p-diamido-diphenylmethane with aniline and some oxidizing agent (B. **25**, 302); by heating p-nitro-benzal chloride with aniline (B. **18**, 997), and by heating aurine to 120° with aqueous ammonia (B. **10**, 1016, 1123).

Nitrous acid converts it into aurine. Triphenyl carbinol results when pararosaniline diazochloride is decomposed with finely divided copper (B. **26**, 2225). At 180–200° pararosaniline is converted by concentrated hydriodic acid into aniline and p-toluidine. Evidence favoring the p-position of the two amido-groups is found in the conversion of p-rosaniline by boiling hydrochloric acid into p_2-diamido-benzophenone, which is also obtained from p-diamido-triphenylmethane, the condensation product of benzaldehyde with aniline. Paraleucaniline, the reduction product from pararosaniline, is also formed by the reduction of p_3-nitrodiamido-triphenyl methane. The p-position of the three groups in the latter compound follows from the fact that it is produced by the same condensation reaction from p-nitrobenzaldehyde and aniline by which p-diamido-triphenylmethane is made from benzaldehyde and aniline.

In addition to the two constitution formulas (I and II) already given for the hydrochloride of pararosaniline, a third (III) may be offered; this would represent it as p_3-triamido-triphenyl carbinol chloride:

I. $\begin{matrix} NH_2 \cdot C_6H_4 \\ NH_2 \cdot C_6H_4 \end{matrix}\!\!>C<\!\!\begin{matrix} C_6H_4NH \cdot HCl \\ \underline{\qquad\quad}| \end{matrix}$ (E. and O. Fischer).

II. $\begin{matrix} NH_2 \cdot C_6H_4 \\ NH_2 \cdot C_6H_4 \end{matrix}\!\!>C = C_6H_4 = NH \cdot HCl$ (Nietzki).

III. $(NH_2 \cdot C_6H_4)_3C \cdot Cl$ . . . . (Rosenstiehl, V. v. Richter).

Also compare B. **29**, 2677, R. 346, in regard to the constitution of the rosaniline bases.

The rosaniline salts give a deeper blue shade than the salts of para-rosaniline (B. **15**, 680).

Homologous Rosanilines have been prepared by the oxidation of a mixture of aniline and unsym. metaxylidine (B. **15**, 1453), by condensation of p-nitrobenzaldehyde with o-toluidine, reduction and oxidation of the resulting condensation product (B. **15**, 679), and by the condensation of p-nitrodimethylamidobenzhydrol with m-toluidine, etc. (B. **24**, 553).

Rosaniline Sulphonic Acid, *Acid Fuchsine, Fuchsine S,* is produced in the action of sulphuric acid at 120° upon rosaniline.

Alkylic Rosanilines.—The introduction of methyl residues into the amido-groups of rosaniline produces violet dyes—*methyl violet.* The violet color assumes a deeper blue tint with the increase of methyl groups. These dyes are made by methylating pararosaniline and by oxidizing dimethyl aniline. The methyl violets are reduced to leuco-compounds when they are heated with ammonium sulphide to 120°. Boiling hydrochloric acid resolves them into dimethyl aniline and methylated p-diamido-benzophenones (B. **19**, 108).

Hexamethyl Pararosaniline, *Crystal Violet,* $[(CH_3)_2N \cdot C_6H_4]_2 \cdot C = C_6H_4 = N(CH_3)_2Cl$, is distinguished from the lower methyl derivatives

by great power of crystallization. It forms one of the principal constituents of methyl violet, and is produced (1) by the condensation of p_2-tetramethyldiamido-benzophenone and dimethyl aniline with dehydrating agents:

$$CO<\begin{matrix}C_6H_4[4]N(CH_3)_2\\C_6H_4[4]N(CH_3)_2\end{matrix} + C_6H_5N(CH_3)_2HCl = C_{19}H_{12}N_3(CH_3)_6Cl + H_2O.$$

(2) By heating dimethylaniline with $COCl_2$ and $AlCl_3$ or $ZnCl_2$ (B. 18, 767; R. 7). Formic acid, formic ester, chlorcarbonic ester, perchlormethyl mercaptan, $CSCl_2$, etc., act the same as phosgene (B. 19, 109); (3) by oxidation of p_2-tetramethyldiamido-diphenyl methane with dimethyl aniline; (4) by heating its methyl chloride or iodide to 110–120°; (5) by oxidizing its leuco-base.

p_3-**Hexamethyl Triamidotriphenyl Carbinol**, *Crystal Violet Base*, $C(OH)[C_6H_4[4]N(CH_3)_2]_3$, melts at 195°.

p_3-**Hexamethyl Triamidotriphenyl Methane**, *Leuco-crystal Violet*, $CH[C_6H_4[4]N(CH_3)_2]_3$, melting at 173°, results by the reduction of *crystal violet*, by the condensation of ortho-formic ester and dimethyl aniline with $ZnCl_2$, and by the condensation of p_2-tetramethyldiamido-benzhydrol with dimethyl aniline.

Methyl Violet is a mixture of hexamethylpararosaniline with lower methylated derivatives (B. **19**, 107). It is produced in oxidizing dimethyl aniline, alone or when mixed with monomethyl aniline, with iodine or chloranil, copper sulphate or chloride. When copper chloride is used it is advisable to add acetic acid or phenol.

Pentamethyl Violet, $C_{19}H_{12}N_3(CH_3)_5HCl$, is formed by oxidizing p_3-**pentamethyltriamidotriphenylmethane**, $[(CH_3)_2NC_6H_4]_2CH.C_6H_4[4]NH.CH_3$, melting at 116°. The latter can be isolated from the reduction-product of commercial methyl violet, a mixture of penta- and hexamethyl violet, by means of the acetyl derivative. This, when oxidized with acetylpentamethyl rosaniline, yields a *green* dyestuff (B. 16, 2906).

Tetramethyl Violet is formed by oxidizing p_3-**amidotetramethyldiamidotriphenylmethane**, melting at 152°. The latter is a **tetramethylparaleucaniline**, $NH_2[4]C_6H_4CH[C_6H_4][4]N(CH_3)_2]_2$, produced in the reduction of p-nitromalachite-green. Its acetyl derivative, like that of pentamethyl-leucaniline, yields a *green* dye upon oxidation.

Methyl Green, *Methyl Chloride of Hexamethyl-pararosaniline Chloride*,

$$Cl(CH_3)_3N[4]C_6H_4C<\begin{matrix}C_6H_4[4]N(CH_3)_2\\C_6H_4[4]N(CH_3)_2Cl\end{matrix},$$

is produced when methyl chloride acts upon an alcoholic solution of methyl violet heated to 40°, sodium hydrate being gradually added.

Alkylic Rosanilines.

When rosaniline is heated with methyl iodide, methyl chloride, ethyl iodide, or chloride, and methyl or ethyl alcohol, three amide hydrogen atoms are replaced by methyl or ethyl radicals. The methyl base yields reddish-violet-colored salts (*Hofmann's Violet, Dahlia*); these dissolve with difficulty in water, but dissolve easily in alcohol.

The violet dyes, by the addition of more methyl or ethyl groups, yield tetra-alkylic rosaniline iodides, which are capable of adding another molecule of methyl or ethyl iodide and forming **iodine greens**—*e. g.*, ***iodmethylate of tetramethyl rosaniline iodide***, $C_{20}H_{16}(CH_3)_4N_3I.CH_3I + H_2O$, which has been displaced in the dye industry by methyl green (see B. **28**, 1008).

Aldehyde Green (Usèbe, J. pr. Ch. **92**, 337), another green rosaniline dye, has been prepared by heating rosaniline with aldehyde and sulphuric acid, and by further action of sodium hyposulphite. The most recent opinion is that in this reaction an aniline group has been changed to quinaldine, while the other two groups have occasioned the formation of aldol aniline residues, which latter then add sulphur, just as is done by aldol aniline itself (p. 79) (compare B. **24**, 1700; **29**, 60).

Phenylated Pararosanilines.—Just as methyl violet is prepared from dimethyl aniline by means of $COCl_2$, etc., so

Diphenylamine Blue can be obtained by heating diphenylamine with carbon hexachloride, C_2Cl_6, or oxalic acid, to 120°. It is identical with *triphenylpararosaniline*, $C(OH)(C_6H_4.NH.C_6H_5)_3$ (B. **23**, 1964), obtained by the action of aniline upon pararosaniline. At present it is only the sodium salts of its mono- and disulpho acids which are applied as *Alkali Blue* and *Water Blue* in dyeing.

Perchlorformic ester, $CClO_2CCl_3$, in a similar manner converts diphenyl methylamine, $(C_6H_5)_2N.CH_3$, into **trimethyl-triphenyl-pararosaniline**,

$C(OH)(C_6H_4.N\left<\begin{smallmatrix}CH_3\\C_6H_5\end{smallmatrix}\right)_3$ (B. **19**, 278). Phosgene converts triphenylamine into the hydrochloride of **hexaphenyl-pararosaniline**, $C(OH)[C_6H_4.N(C_6H_5)_2]_3$ (B. **19**, 758).

Tricarbazole Carbinol, $C(OH)(C_{12}H_7NH)_3$ (B. **20**, 1904), is produced by heating together carbazole and oxalic acid. It is analogous to the triphenylamine derivative.

Phenylated Rosanilines are obtained by heating rosaniline hydrochloride with aniine or toluidines, or the free base with aniline and some benzoic acid. The **triphenylrosaniline hydrochloride**, $C_{20}H_{16}(C_6H_5)_3N_3.HCl$, appeared in commerce as *aniline blue*, a bluish-brown crystalline powder with copper luster, soluble in alcohol but not in water. To dissolve it in the latter, sulpho salts are prepared, which exhibit different shades of blue (*soluble blue*) corresponding to the number of sulpho-groups in them. At present diphenylamine blue and other dyes have taken its place. Diphenylamine results on distilling triphenyl-rosaniline.

By converting rosaniline, by means of the tridiazo-compound into the *trihydrazine* derivative, there results *Roshydrazine*, $C(OH)(C_6H_5.NH.NH_2)_3$; this, by condensation with aldehydes and ketones, yields red and blue dyestuffs (B. **20**, 1557).

3. **Phenol Derivatives of the Triphenylmethanes.**—The phenol derivatives of the triphenylmethanes are produced (1) from the corresponding amido-compounds through the diazo-derivatives; (2) by condensations similar to those of the amido-compounds if phenols be substituted for the anilines; (3) by the reduction of the phenol carbinols, into which they are changed by oxidation.

Monoxytriphenyl Methanes.—In this class may be included o-**Diphenyl Cresol**, o-*Oxytriphenyl Methane*, $(C_6H_5)_2CH.C_6H_4[2]OH$, melting at 118°. It is obtained from o-amidotriphenyl methane (A. **241**, 367). *Oxydiamidotriphenyl Methanes* (B. **14**, 2522; **16**, 1307) are produced by the condensation of salicylaldehyde and anisaldehyde with aniline sulphate or dimethyl aniline and zinc chloride.

The di- and **tri-oxytriphenyl methanes** yield, on oxidation, di- and triphenol carbinols, which, as a rule, possess the character of dye-substances. Carbinols in which two benzene nuclei are hydroxylated, and which correspond to the malachite-green compounds, are termed ***benzeïnes***; whereas the derivatives with three hydroxylated benzene nuclei are called ***aurines*** or ***rosolic acids***, while corresponding trioxytriphenylmethanes are designated as ***leucaurines*** or ***leuco-rosolic acids***.

p_2-Dioxy-triphenyl Methane, *Leucobenzeïne*, leucobenzaurine, $C_6H_5.CH(C_6H_4[4]OH)_2$, is obtained (1) from p_2-diamido-triphenyl methane (p. 352) (A. **206**, 153)

(2) by reducing benzaurine (A. **217**, 230), as well as (3) by the condensation of benzaldehyde and phenol with sulphuric acid (B. **22**, 1944). It melts at 161°.

Dioxydimethyl Triphenyl Methane, $C_6H_5CH[C_6H_3(OH)CH_3]_2$, melts at 170° (A. **257**, 70). **Phenyldithymol Methane** melts at 166°.

See B. **24**, R. 562, for the condensation of m-nitrobenzaldehyde with phenols.

p_3-**Trioxy-triphenyl Methane, Leucaurine,** [*Triphenylol Methane*], $CH(C_6H_4[4]\text{-}OH)_3$, is obtained in the reduction of aurine, its carbinol anhydride, by means of zinc-dust and sodium hydrate or acetic acid. It crystallizes in colorless needles, which become colored on exposure to the air (A. **166**, 286; **194**, 136; **202**, 198). The *triacetate* melts at 138° (B. **11**, 1117).

Leuco-rosolic Acid, $(HO[4]C_6H_4)_2.CH.C_6H_3[4]OH[3]CH_3$, results from the reduction of rosolic acid. Its *triacetate* melts at 148° (A. **179**, 198).

4. **Phenol Derivatives of Triphenyl Carbinol.**—A. **Benzeïnes** (see above) are produced by the condensation of benzotrichloride with mono- and polyhydric phenols, in which the para-position with reference to a hydroxyl group is not substituted—*e. g.*, o- and m-cresol, resorcinol, and pyrocatechin (but not p-cresol, hydroquinone, etc.) (B. **23**, R. 340). They are also formed when their leuco-compounds, the corresponding oxytriphenyl methanes, are oxidized.

The benzeïnes are generally red-colored compounds with metallic luster. They dissolve on boiling with sodium bisulphite; acids reprecipitate them. Alkalies dissolve them with the formation of red or violet-colored salts. The carbon dioxide of the air decomposes the latter.

p_2-**Dioxy-triphenyl Carbinol,** *Phenol Benzeïne, Benzaurine*, $C_6H_5.C{<}^{C_6H_4.OH}_{C_6H_4.O}$ (with the C and O joined)

or $C_6H_5.C{<}^{C_6H_4.OH}_{C_6H_4=O}$, is produced in the condensation of benzotrichloride and phenol (similar to the formation of malachite-green) (A. **217**, 223), and by the oxidation of p-dioxytriphenylmethane, into which it passes upon reduction. It is a brick-red, crystalline powder. It breaks down, when fused with alkalies, into benzene and dioxybenzophenone, and this latter decomposes further into paraoxybenzoic acid and phenol. Its *diacetate* melts at 119°.

p_2-**Dioxy-**m_2-**dimethyl Triphenylmethane,** o-Cresol Benzeïne, $C_6H_5.C(OH).[C_6H_3[3]CH_3[4]OH]_2$, melts at 220–225° (A. **257**, 69).

Resorcinol Benzeïne, $C_{38}H_{30}O_9 = \begin{matrix} C_6H_5C[C_6H_3(OH)_2]_2 \\ | \\ O \\ | \\ C_6H_5C[C_6H_3(OH)_2]_2 \end{matrix}$, is formed when water acts upon the reaction product of resorcinol and benzotrichloride (A. **217**, 234), and when $ZnCl_2$ acts upon benzoic acid and resorcin (J. pr. Ch. [2], **48**, 387). See B. **26**, 2064, for dinitroresorcinol benzeïne.

Rosamines.—These are derivatives of diamido-benzeïnes. They are formed when mono-alkylic and dialkylic o-amidophenols act upon benzotrichloride. While the benzeïnes, from phenols, are very feeble dyes, whose alkali salts are even decomposed by carbon dioxide, the hydrochlorides of the rosamines are red and violet dyes, having great similarity to the rhodamines (p. 366), but possessing a blue tint and redder fluorescence (B. **22**, 3001). They also result on heating resorcinol benzeïne with dimethyl and diethyl aniline.

Rosamine Chloride, $C_6H_5C{<}^{C_6H_3\{^{[4]N(CH_3)_2}_{[2]}}_{C_6H_3\{^{[2]}_{[4]N(CH_3)_2Cl}}$ ([2] positions joined by >O; C joined to the N), may be obtained from benzotrichloride and dimethyl aniline. It forms reddish-black needles with a steel-blue reflex.

B. **Aurines and Rosolic Acids.**—These compounds correspond perfectly to the rosanilines The free p_3-trioxy-triphenyl carbinols are not known. When freed from their salts they sustain an intramolecular anhydride formation.

These carbinol anhydrides are yellow in color; their alkali salts dissolve in water,

with a red color. They are incompletely fixed by the fiber of the material, and are only applied in the form of lakes in the paper industry.

Aurine, Para-rosolic Acid, *Yellow Corallin,* $\begin{matrix}HO[4]C_6H_4\\HO[4]C_6H_4\end{matrix}>C<\frac{C_6H_4[4]}{\quad}>O$, is produced (1) on boiling the diazohydrochloride of pararosaniline with water (A. **194**, 301); (2) by the condensation of p-dioxybenzophenone chloride with phenol (B. **11**, 1350); (3) by the condensation of phenol with formic acid on heating with zinc chloride (J. pr. Ch. [2], **23**, 549); and (4) by heating phenol (1 part) with oxalic (⅔ part) and sulphuric (½ part) acids to 130–150° (A. **202**, 185). For the by products arising when aurine is prepared by method 4, and for its separation from the same, see A. **194**, 123; **196**, 77; B. **28**, R. 743.

Aurine dissolves in glacial acetic acid and alcohol, crystallizes in dark red needles or prisms with metallic luster, and decomposes when heated above 220°. It dissolves in alkalies with a fuchsine-red color. With the primary alkaline sulphites it readily yields colorless, crystalline derivatives, decomposable by acids and alkalies. Aurine forms crystalline compounds with hydrochloric acid. Water decomposes them. Digested with *zinc-dust and hydrochloric acid or acetic acid, aurine is reduced to leucaurine or* p_3*-trioxy-triphenylmethane.* Heated to 250° with water, it breaks up into p_2-dioxybenzophenone and phenol.

Aurine is changed to pararosaniline when it is heated with aqueous ammonia to 150°. An intermediate product (having 1 or 2 amide groups) is the so-called *Peonine* (red corallin). With aniline we obtain triphenyl-rosaniline, and the intermediate product is *Azuline.* Consult B. **29**, R. 510, for isomeric *acetyl-aurines.*

Rosolic Acid, $C_{20}H_{16}O_3$, is the inner anhydride of p_3-*trioxydiphenyl*-m-*tolylcarbinol.* Rosolic acid, like aurine, is obtained by boiling the diazochloride of rosaniline with water (A. **179**, 192) and by oxidizing a mixture of phenol and cresol, $C_6H_4(CH_3)OH$, with arsenic acid and sulphuric acid, whereby the linking methane carbon is furnished by the methyl group. When rosolic acid is digested with alcohol and zinc-dust, it is reduced to leucorosolic acid, from which it is obtained by oxidation (B. **26**, 254).

Trioxy-aurine, $C_{19}H_{14}O_6$, results from the interaction of $ZnCl_2$, pyrocatechine, and formic acid (B. **26**, 255). **Resaurine,** $C_{19}H_{14}O_6$, is similarly prepared with resorcinol (J. pr. Ch. [2], **23**, 547). **Orcin-aurine,** $C_{22}H_{18}O_5$ (J. pr. Ch. [2], **25**, 277; B. **13**, 546).

Eupittonic Acid, *Eupitton, Hexamethoxy-aurine,* $C_{19}H_8(OCH_3)_6O_3$, is produced by oxidizing a mixture of the dimethyl ester of pyrogallic acid and methyl pyrogallic acid. *It is, therefore, an aurine in which six methoxyl groups are present.* It forms orange-yellow crystals, melting with decomposition at 200°. It dissolves with a deep blue color in alkalies, yielding salts which are precipitated by excess of alkali (B. **12**, 2216). Reichenbach (1835) observed the formation of a blue-colored barium salt when fractions of beechwood-tar were allowed to stand with baryta-water, and named it *pittical* (from πίττα, tar, and κάλλος, beautiful). When heated with ammonia, eupittonic acid, just like aurine, affords an *hexamethoxyl-rosaniline.*

5 and 6. **Alcohols and Aldehydes of Triphenylmethane.**—Few of them are known: **Phenolphthalol,** $(HOC_6H_4)_2CHC_6H_4[2]CH_2OH$, melting at 190°, was prepared by the action of sodium amalgam upon phenolphthaleïn (A. **202**, 87).

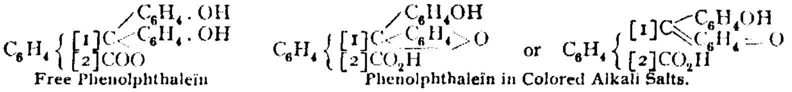
p-Diphenylmethyl-benzaldehyde, $(C_6H_5)_2CH[4]C_6H_4 . CHO$, boiling at 190–195° (46 mm.), results from the condensation of terephthalaldehyde and benzene with concentrated sulphuric acid (B. **19**, 2029).

7. **Carboxyl Derivatives of Triphenylmethane.** — **Triphenylmethane Carboxylic Acids** are produced (1) by reduction of triphenyl carbinol carboxylic acids, and (2) from their nitriles. The latter are prepared by the action of aluminium chloride upon the cyanbenzal chlorides (p. 238) and benzene.

Triphenylmethane-o-carboxylic Acid, *Benzene Phthalin* (see phthaleïns, p. 363), $(C_6H_5)_2CH . C_6H_4[2]CO_2H$, melting at 162°, is isomeric with triphenyl acetic acid (p. 369), and is produced by the reduction of diphenylphthalide (2), the lactone of triphenylcarbinol-o-carboxylic acid (A. **202**, 52), and from its nitrile. Chromic acid oxidizes it to diphenylphthalide, while it breaks down into carbon dioxide and triphenylmethane when it is heated with barium hydroxide. Sulphuric acid rearranges it to phenylanthranol (3):

trated caustic alkali causes the colors to disappear. On diluting with water, the colors reappear.

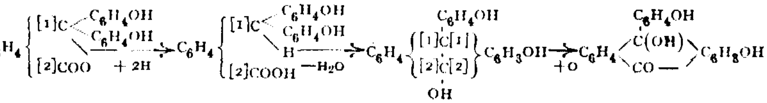
To show the similarity of the phthaleïns to the aurines or rosanilines in the formula, it is assumed that the free, colorless phthaleïns contain the lactone ring; in their colored alkali salt solutions this ring is absent, and the methane carbon atom and an oxygen atom form a quinone-like union with a benzene nucleus. This idea is apparently supported by the preparation of phthaleïnoxime:



Free Phenolphthaleïn — Phenolphthaleïn in Colored Alkali Salts.

It should also be added that lactone esters and ethers have also been obtained by acidylation and alkylization of phenolphthaleïn in alkaline solution (B. **28**, 3258; **29**, 131; compare B. **29**, R. 552).

The phenolphthaleïns, by reduction, yield oxytriphenylmethane carboxylic acids—the *phthalins* (p. 361). The latter are changed by concentrated sulphuric acid into oxyphenylanthranol derivatives, called *phthalidines*. The oxidation of the latter produces the *phthalideïnes*, or oxyphenyloxanthranol derivatives. The following diagram represents these changes, with phenolphthaleïn as the example:



Phthaleïn, p_2-Dioxydiphenyl-phthalide — Phthalin, p_2-Dioxytriphenyl-methane-o-carboxylic Acid — Phthalidin, Dioxyphenyl-anthranol — Phthalideïn, Dioxyphenyl-oxanthranol.

Phenolphthaleïn, p_2-*Phthaleïn*, *Dioxydiphenyl-phthalide*, $C_{20}H_{14}O_4$, is a yellow powder, crystallizing from alcohol in colorless crusts, and melting at 250°. It dissolves in the alkalies with a red color It is used as an indicator in alkalimetry, especially in determining carbon dioxide with baryta (B. **17**, 1907). It is formed from phthalophenone when nitrous acid acts on the p-diamido compound; by oxidizing an alkaline solution of the corresponding phthalin with air, or with potassium ferricyanide or potassium permanganate, and is also obtained on heating phthalic anhydride with phenol and tin chloride, or with sulphuric acid to 115–120° for eight hours. o_2-Dioxydiphenylphthalide anhydride, insoluble in caustic potash, is a by-product. Boiling caustic potash and zinc-dust reduce phthaleïn to phthalin (p. 361), and it is decomposed into p_2-dioxybenzophenone and benzoic acid by fusion with caustic potash (A. **202**, 68).

Lactone Derivatives of Phenolphthaleïn: Diacetophenolphthaleïn melts at 143°. **Dibenzoylphenolphthaleïn** melts at 169° (B. **29**, 131). **Dimethyl Phenolphthaleïn**, melting at 98° (B. **29**, 138, R. 848), has also been obtained synthetically from phthalic anhydride, anisol, and Al_2Cl_6 (B. **29**, R. 550). **Phenolphthaleïn Anilide**, $C_6H_4\left\{\begin{matrix}[1]C=(C_6H_4.OH)_2 \\ \diagdown \\ [2]CONC_6H_5\end{matrix}\right.$, melts at 279° (B. **26**, 3077). **Tetrabromphenolphthaleïn**, $C_{20}H_{10}Br_4O_4$, melts with decomposition at 220–230°.

The colored alkali salts are *quinoid derivatives of phenolphthaleïn*.

In this class is also—

Phenolphthaleïn Oxime, $C_6H_4\left\{\begin{matrix}[1]C\begin{matrix}\diagup C_6H_4.OH \\ \diagdown C_6H_4=N.OH\end{matrix} \\ [2]CO_2H\end{matrix}\right.$, a yellow crystalline pow-

der, melting with decomposition at 221°, and produced by the action of hydroxylamine upon an alkaline phenolphthaleïn solution. Boiling, dilute sulphuric acid decomposes the oxime into p-oxy-o-benzoylbenzoic acid and p-amidophenol (B. **26**, 172). **Tetrabromphthaleïn Oxime** (B. **26**, 2260). See B. **30**, 176, upon the quinoïd **tetrabromphenolphthaleïnmono- and -diethyl ethers.**

Fluorane, o_2-*Phenolphthaleïn Anhydride*, $C_6H_4\left\{\begin{matrix}[1]C\begin{matrix}\diagup C_6H_4[2] \\ \diagdown C_6H_4[2]\end{matrix}\Big\}O \\ [2]COO\end{matrix}\right.$, melting at 173–175°, is produced, together with p_2-phenolphthaleïn, by the condensation of phthalic anhydride and phenol. Fluorane yields hydrofluoranic acid by reduction (p. 362), and diphenylenephenylmethane when it is distilled over zinc-dust (B. **25**, 3586). The *anil*, $C_6H_4\left\{\begin{matrix}[1]C = (C_6H_4)_2O \\ \diagdown \\ [2]CON\,.\,C_6H_5\end{matrix}\right.$, melts at 242° (B. **27**, 2793). **Tribromfluorane,** $C_{20}H_{19}Br_3O_3$, melting at 298–300°, is produced by the action of PBr_5 upon fluoresceïn, and is reduced by alcoholic caustic soda and zinc-dust to hydrofluoranic acid (B. **25**, 1388).

The **fluoresceïns** are the o-phthalic anhydrides produced by the condensation of phthalic anhydrides with resorcinol. They are characterized by a beautiful fluorescence; this is especially true of their alkaline solutions (Baeyer, A. **183**, 1).

Phthalic anhydride may also be replaced by the anhydrides of aliphatic dicarboxylic acids. When succinic, maleïc, and citraconic anhydrides are condensed with resorcinol, the corresponding fluoresceïns are produced. See also naphthalic acid (B. **15**, 883; **18**, 2864; **24**, R. 763; **26**, R. 542; **29**, 2824).

Resorcinol-phthaleïn, Fluoresceïn, $C_{20}H_{12}O_5$, is prepared by heating phthalic anhydride (2 parts) with resorcinol (7 parts) to 200°, or with anhydrous oxalic acid (B. **17**, 1079) to 110–117°. When precipitated from its salts it is a yellowish-red powder, $C_{20}H_{14}O_6$, which quickly loses water and becomes $C_{20}H_{12}O_5$, which dissolves in alcohol with a yellow-red color and green fluorescence. Its concentrated alkali solution is dark red, but on dilution it gradually becomes yellow, and then exhibits a magnificent yellowish-green fluorescence. Upon reduction fluoresceïn yields fluorescine (p. 362), and PCl_5 converts it into fluoresceïn chloride, p_2-dichlorfluorane (see rhodamines, p. 366 (A. **183**, 18).

Baeyer ascribes the formula $C_6H_4\left\{\begin{matrix}[1]C = (C_6H_3OH)_2O \\ \diagdown \\ [2]COO\end{matrix}\right.$ to fluoresceïn. As there was a disposition to assume that the phthalic acid residue replaced both m-hydrogen atoms (5) in the resorcinol molecules, R. Meyer showed that fluoresceïn is a dioxy-derivative of o-phenolphthaleïn anhydride, for which reason he gave it the name **fluorane** (above); that, therefore, the phthalic acid residue occupied the o-position with reference at least to each of the hydroxyl groups of the resorcinol molecule, and between these hydroxyl groups the anhydride formation occurred. R. Meyer converted fluoresceïn (1) by means of PBr_5 into tribromfluorane (2), which, like fluorane (4) itself, yields hydrofluoranic acid (3) upon reduction. Fluoresceïn and fluorane contain a ring closely related to the xanthone ring; indeed, hydrofluoranic acid (p. 362) may be decomposed into xanthone and benzene:

$$\overset{(1)}{C_6H_4\left\{\begin{matrix}[1]C\begin{matrix}\diagup C_6H_3(OH)[2] \\ \diagdown C_6H_3(OH)[2]\end{matrix}\Big\}O \\ [2]COO\end{matrix}\right.} \rightarrow \overset{(2)}{C_{20}H_9Br_3O_2} \rightarrow \overset{(3)}{C_6H_4\left\{\begin{matrix}[1]CH\begin{matrix}\diagup C_6H_4 \\ \diagdown C_6H_4\end{matrix}\!>O \\ [2]COOH\end{matrix}\right.} \leftarrow \overset{(4)}{C_6H_4\left\{\begin{matrix}[1]C\begin{matrix}\diagup C_6H_4 \\ \diagdown C_6H_4\end{matrix}\!>O \\ [2]COO\end{matrix}\right.}$$

The intense color of fluoresceïn led Bernthsen and others to ascribe a quinoïd constitution to free flouresceïn and its colored derivatives (see phenolphthaleïn). The colorless derivatives were supposed to have their origin in the lactone formula of fluoresceïn. This view allies fluoresceïn and its colored derivatives with the aurines and rosanilines.

When fluoresceïn is fused with caustic soda it breaks down into resorcinol and monoresorcinol phthaleïn, or dioxybenzoylbenzoic acid. Bromine in glacial acetic acid changes the latter to dibromodioxybenzoylbenzoic acid, which fuming sulphuric acid rearranges to dibromxanthopurpurine; it is also obtained from eosin. Hence it follows that monoresorcinol phthaleïn is 2,4-dioxy-o-benzoylbenzoic acid, because if it were 2,6-dioxy-o-benzoylbenzoic acid it would be impossible for an anthraquinone condensation to occur (Heller, B. **28**, 314; B. **29**, 2623).

Lactone Derivatives of Fluoresceïn.—**Fluoresceïn Anilide**, $C_{20}H_{17}NO_4$. The *dimethyl ether* is colorless, melts at 207°, and when boiled with sulphuric acid changes to colorless **fluoresceïn dimethyl ether**, melting at 198° (B **28**, 396).

Quinoïd Derivatives of Fluoresceïn.—**Fluoresceïn Carboxyl Ethyl Ether**, melting at 247°, is produced by the oxidation of **fluoresceïn ethyl ether**, melting at 196° (p. 362), and consisting of crystals with a green luster. An alcoholate and ethyl bromide convert fluoresceïn carboxyl ethyl ether into the *colored* **diethyl ether**, melting at 159°. This forms dark yellow needles. The **dimethyl ether**, melting at 208°, is made from fluoresceïn by the action of methyl alcoholic potash and methyl iodide (B. **28**, 396; B. **29**, R. 848).

Substituted Fluoresceïns.—Although fluoresceïn itself is not applicable as a dye, by introducing halogens and nitro-groups into it dyestuffs of remarkable beauty can be obtained. If we start with fluoresceïn, then the substitution will occur in the resorcinol residues.

If bromine be allowed to act on fluoresceïn suspended in glacial acetic acid, **Eosin, Tetrabromfluoresceïn**, $C_{20}H_8Br_4O_5$, is produced. Crystallized from alcohol it forms red crystals. The *potassium* and *sodium salts* constitute the eosin of commerce, soluble in water, and imparting to wool and silk a beautiful rose-color. In the case of the sodium salt there is a yellowish-red fluorescence (Caro, 1873).

Erythrosine, *Tetraiodfluoresceïn*, $C_{20}H_8I_4O_5$.

Safrosine, *Eosin Scarlet*, Dibromdinitrofluoresceïn, $C_{20}H_8Br_2(NO_2)_2O_5$, is formed when bromine acts upon dinitrofluoresceïn, or when nitric acid acts upon di- or tetrabromfluoresceïn (A. **202**, 68). See B. **30**, 333, for the dinitrofluoresceïn yellow from dinitrofluoresceïn and ammonia.

To obtain the fluoresceïns substituted in the phthalic acid residue, condense the chlorinated phthalic anhydrides with resorcinol (Noelting). The brom- and iodfluoresceïns, with the substituents in the resorcinol residues, are at the same time prepared from the chlorinated bodies:

Phlorine, *Tetrabromdichlor-* and *Tetrabromtetrachlorfluoresceïn*, $C_{20}H_4Cl_4Br_4O_5$,
Rose Bengal, *Tetraiodtetrachlorfluoresceïn*.

Phthalic anhydride has also been condensed with pyrocatechol (B. **22**, 2197), *hydroquinones*, *orcins*. and *phloroglucin*.

Pyrogallol-phthaleïn, Galleïn, $C_{20}H_{10}O_7$, is obtained on heating pyrogallic acid with phthalic anhydride to 200°. It forms crystals with green color, dissolving with a dark red color in alcohol and with a beautiful blue color in the alkalies.

It is converted by concentrated sulphuric acid into *Coeruleïn* (see A. **209**, 249).

The **rhodamines**, the phthaleïns of m-amidophenol and its derivatives, are of special importance. They are violet-red, magnificently fluorescent dyestuffs. In constitution they are perfectly analogous to the fluoresceïns.

The *simplest* rhodamine is formed when m-amidophenol hydrochloride and phthalic anhydride are heated to 190° with concentrated sulphuric acid (B. **21**, R. 682).

The alkylic rhodamines possess more intense colors. They are produced when rhodamine hydrochloride is heated with alkyl iodides. A better course to pursue is the condensation of alkylic m-amidophenols and phenyl-m-amidophenol with phthalic anhydride (B. **21**, R. 682, 920; **22**, R. 788). Still another procedure consists in rearranging fluoresceïn chloride, melting at 252° (the product of the action of PCl_5 upon fluoresceïn), by heating it with dialkylamines (B. **22**, R. 625, 789).

Anisolines, alkyl ethers of the rhodamines (?)—see B. **25**, R. 866.

Succino-rhodamine has been obtained from succinic anhydride and m-amidophenol (B. 23, R. 532).

All that has been said relative to the constitution of the fluoresceïns applies to the rhodamines. The nomenclature of the fluoresceïns can be greatly simplified if the bodies having the atomic group $-C\langle^{C_6H_4}_{C_6H_3=O}\rangle O$ are designated **fluorones**, and those with the atomic group $-C\langle^{C_6H_4}_{C_6H_3=NH}\rangle O$, **fluorimes** (B. 27, 2987).

Consult B. 28, 2959, for the orcin phthaleïns and hydroquinone phthaleïns. Hydroquinone phthaleïn does not behave like fluoresceïn, hence probably does not contain the fluorane residue which is present in the latter compound. The condensation of phthalic anhydride with orcinol and sulphuric acid or P_2O_5 gives rise to three orcinol phthaleïns. It is only that orcinol phthaleïn, however, which contains the two hydroxyl groups in the p-position *with reference to the* phthalic acid *residue which is the* perfect **analogue** *of* fluoresceïn (B. 29, 2630).

IV. DIPHENYL ETHANE GROUP.

Homologous series are derived from diphenylmethane. Dismissing the substitutions in the benzene residues, this is attained by replacing the H-atoms of the methylene residue by alkyl groups: diphenylmethyl-, diphenyldimethyl-, diphenylethyl-, diphenylpropylmethane, etc.; and, again, it can be done by inserting new C-atoms between the two benzene residues: *ω,ω*-diphenyl ethane or dibenzyl, *ω,ω*-diphenyl propane, *ω,ω*-diphenyl butane, *ω,ω*-diphenyl pentane, etc. A sharp division is impossible, because of the unequal experimental investigation of the material. The group of unsym. diphenylethane or diphenylmethylmethane will receive first attention in the following paragraphs; its members attach themselves in their deportment to diphenylmethane and its derivatives; at the same time they show in many ways their genetic relationship to the dibenzyl group. Compare benzilic acid, diphenylacetaldehyde, stilbene, tolane.

After these there will follow the important dibenzyl or sym. diphenylethane group, and then the *ω,ω*-diphenyl-, propane-, butane-, pentane-, and hexane-groups. The derivatives alkylized or phenylated in the benzene nuclei, or in the side-chains connecting these, are included with the parent hydrocarbons of the individual groups; the saturated are followed by the unsaturated hydrocarbons.

A. Unsym. **Diphenyl Ethane Derivatives** are, as a rule, formed by the condensation of aldehyde, chlorinated aldehydes, glyoxylic acid, etc., with benzene hydrocarbons, phenols, or tertiary anilines, just as the diphenylmethanes (p. 342) are produced by means of methylal, methylene iodide, etc.:

$$CH_3 . CHO + 2C_6H_6 \longrightarrow CH_3CH(C_6H_5)_2 + H_2O.$$

All the substances included in this class yield *benzophenone* or its derivatives when they are oxidized.

Unsym. **Diphenyl Ethane**, $(C_6H_5)_2CHCH_3$, boiling at 209° (145° at 13 mm.), is made from benzene and paraldehyde with cold sulphuric acid; also from ethidene chloride, CH_3CHCl_2, sym. brom-ethyl benzene, $C_6H_5 . CHBr . CH_3$, or styrene with benzene and Al_2Cl_6. Chromic acid oxidizes it to benzophenone, with the elimination of the methyl group. Consult B. 27, 3238. Nitric acid nitrates the side-chains and not the

benzene residues of unsym. diphenyl-ethane. The products are: **Diphenylethylene glycol mononitrite**, $(C_6H_5)_2C(OH).CH_2(ONO)$, melting at 100°, **diphenylvinyl nitrite**, $(C_6H_5)_2C=CH(ONO)$, melting at 86°, and a **dinitrite** melting at 148–149°. The latter is probably a diphenyl-ethylene derivative. These three compounds have great crystallizing power. They form yellow crystals, and when oxidized yield benzophenone (A. **233**, 330).

Unsym. **Phenol Phenylethane**, $C_6H_5CH(CH_3)C_6H_4.OH$, melting at 58°, is produced when sulphuric acid acts upon phenol and styrene; the homologous phenols, naphthols, etc., behave similarly toward styrol (B. **24**, 3891). Unsym. **diphenolethane**, $(C_6H_4OH)_2CHCH_3$, melting at 122°, can be obtained from aldehyde and phenol (B. **19**, 3009).

Unsym. **Diphenyl Monochlor-ethane**, $(C_6H_5)_2CH.CH_2Cl$, is an oil. **Diphenyl Dichlor-ethane**, $(C_6H_5)_2CH.CHCl_2$, melting at 80°, and **Diphenyl Trichlor-ethane**, $(C_6H_5)_2CH.CCl_3$, melting at 64°, are obtained from mono-, di-, and trichloracetaldehyde (chloral) with benzene and sulphuric acid. Alkali, acting upon these substances, splits off hydrogen chloride, and the products are:

Unsym. **Diphenyl Ethylene**, $(C_6H_5)_2CH:CH_2$, melting at 44° and boiling at 277°, which can also be formed from unsym. dibromethylene, $CBr_2:CH_2$, with benzene and Al_2Cl_6; **diphenylmonochlor-ethylene**, $(C_6H_5)_2C:CHCl$, melting at 42° and boiling at 298°, and **diphenyldichlorethylene**, $(C_6H_5)_2C:CCl_2$, melting at 80° and boiling at 316°, which is also found in the condensation products of chloral with benzene and aluminium chloride (B. **26**, 1955). If diphenylmonochlor-ethane be heated alone it splits off hydrochloric acid and is rearranged to **stilbene** (p. 369). The latter is similarly produced by the reduction and rearrangement of diphenyltrichlorlethane with zinc-dust and alcohol. When diphenylmonochlor-ethylene is heated with a sodium ethylate solution it is transformed into **tolane** (p. 370). **Diphenylvinyl Ethyl Ether**, $(C_6H_5)_2C:CHOC_2H_5$, is formed simultaneously:

$$(C_6H_5)CH.CH_2Cl \xrightarrow{-HCl} C_6H_5.CH:CH.C_6H_5$$
$$(C_6H_5)_2CH:CHCl \xrightarrow{-HCl} C_6H_5.C:C.C_6H_5.$$

These transposition reactions have been extended to a series of substituted diphenylmono- and trichlor-ethanes and to diphenylmonochlorethylene (A. **279**, 319; B. **26**, R. 270).

When diphenylvinyl ether is saponified with glacial acetic acid and hydrochloric acid it does not yield diphenylvinyl alcohol, but **diphenylacetaldehyde**, $(C_6H_5)_2CH.CHO$, boiling at 168–172° (28 mm.). The *oxime* melts at 120°. The aldehyde in many respects deports itself analogously to the oxymethylene derivatives—*e. g.*, when it is oxidized it does not change to the acid, but splits off the CHO-group and becomes benzophenone (B. **24**, 1780; **25**, 1781). Diphenylacetaldehyde is also formed from the hydrobenzoïns by dehydrating agents. Anhydrides of the hydrobenzoïns are formed at the same time:

$$C_6H_5.CH.OH.CH.OHC_6H_5 \xrightarrow{-H_2O} (C_6H_5)_2CH.CHO.$$

This is due to an atomic rearrangement opposite to that of the transpositions of the unsym. diphenylchlor-ethanes and ethylenes just indicated. It reminds one of the pinacoline rearrangement of the pinacones.

Diphenyl Acetic Acid, $(C_6H_5)_2CH.CO_2H$, is formed from its cyanide; and by reducing benzilic acid with hydriodic acid and phosphorus in glacial acetic acid (A. **275**, 84). The acid melts at 146°. When oxidized with a chromic acid mixture it yields benzophenone; and when heated with soda lime we get diphenyl methane. Its *ethyl ester* melts at 58°; the *methyl ester* at 60°.

Diphenylacetonitrile, $(C_6H_5)_2CH.CN$, results when diphenylbrommethane is heated with $Hg(CN)_2$, or by the condensation of mandelic nitrile, $C_6H_5.CH(OH)CN$, and benzene with tin tetrachloride (B. **25**, 1615). It melts at 72° and boils at 184° (at 12 mm.). The hydrogen of its CH-group is readily replaced by the benzene residue, but not by alkyls (A. **275**, 87). **Iodine, acting upon its sodium derivatives, produces tetraphenyl-succino-nitrile.**

Tetranitro-diphenyl Acetic Acid, $\frac{C_6H_3(NO_2)_2}{C_6H_3(NO_2)_2}>CH.CO_2H$.

The *ethyl ester* is derived from dinitro-phenyl-acetoacetic ester and dinitro-phenyl-malonic ester (pp. 258, 259) by the action of o,p-dinitrobrombenzene; the group CO. CH_3 (and $CO_2.C_2H_5$) being replaced. It may be similarly prepared from dinitro-phenyl-acetic ester by the introduction of the dinitro-phenyl residue. It melts at 154°. Alcoholic potash or soda converts the ester, by the substitution of the hydrogen of the CH-group, into brilliant metallic salts, dissolving in alcohol and water, with *a dark blue color*. Compare tetranitro-phenylmethane, $[(C_6H_3NO_2)_2]CH_2$ (p. 343) and trinitrotriphenyl methane $(C_6H_4NO_2)_3CH$ (p. 352) (B. **22**, 2476).

The lactone of a **tetraoxydiphenylacetic acid,** $COOH.CH[C_6H_3(OH)_2]_2$, has been obtained by the condensation of chloral with resorcinol by means of potassium bisulphate. It has a yellow color. It dissolves in cold alkalies with a red color, and forms a *triacetyl derivative*, melting at 152° (B. **29**, R. 776).

Benzilic Acid, Diphenyl Glycollic Acid, $(C_6H_5)_2C(OH).CO_2H$, melting at 150°, is produced by a molecular rearrangement of benzil (see this) when digested with alcoholic potassium hydroxide, and from diphenyl acetic acid by the action of bromine and boiling with water. We can prepare it better by the action of aqueous potash and air upon benzoïn (B. **19**, 1868).

$$C_6H_5.CO.CO.C_6H_5 \xrightarrow{H_2O} (C_6H_5)_2C(OH)COOH.$$

When heated above its melting point benzilic acid takes on a blood-red color and dissolves with the same color in sulphuric acid. Diphenylenediphenylethane derivatives are produced by the action of concentrated sulphuric acid upon benzilic acid (B. **29**, 734). It yields diphenyl acetic acid when heated with hydriodic acid and phosphorus. On distilling its barium salt it breaks up into carbon dioxide and benzhydrol; oxidation yields benzophenone.

Anisilic Acid, $(CH_3OC_6H_4)_2C(OH)COOH$, *Cuminilic Acid*, $(C_3H_7C_6H_4)_2C(OH)$.COOH. and *Hexamethoxybenzilic Acid*, $[(CH_3O)_3C_6H_2]_2C(OH)COOH$, are prepared, like benzilic acid, from their corresponding substituted benzils (p. 375).

β,β-Diphenyl Propionic Acid, $(C_6H_5)_2CH.CH_2.COOH$, is a homologue of diphenylacetic acid. It melts at 149°. It is formed by the addition of benzene to cinnamic acid. This is accomplished by means of sulphuric acid, just as phenol-phenylethane is obtained from styrol and phenol (p. 368). The continued action of the sulphuric acid leads to a condensation to γ-phenylhydrindone (p. 387). Phenyltolyl-, phenylxylyl-propionic acids, etc., are prepared just like diphenylpropionic acid (B. **26**, 1579). Potassium permanganate oxidizes these acids to benzophenone, phenyltolylketone, phenylxylylketone, etc.

γ-Diphenylitaconic Acid, $(C_6H_5)_2C:C(COOH).CH_2.COOH$, is obtained by the condensation of benzophenone with succinic ester through the agency of sodium ethylate (B. **30**, 94).

Triphenyl Acetic Acid, $(C_6H_5)_3C.COOH$, is a very feeble acid. It melts at 264° and decomposes into triphenylmethane and carbon dioxide. It is isomeric with the previously described triphenylmethane carboxylic acids. It is made by the action of benzene and aluminium chloride upon trichloracetic acid, and when carbon dioxide is conducted over potassium triphenylmethane (p. 357) at 200°. The best procedure consists in using the *nitrile*, $(C_6H_5)_3C.CN$, melting at 127°; the latter is produced by the interaction of triphenylchlor- or -brom methane (p. 353) and mercuric cyanide, $Hg(CN)_2$ (A. **194**, 260; B. **28**, 2782), or by deamidizing hydrocyanpararosaniline (B **26**, 2225).

p_3-**Triamido-triphenyl-acetic Nitrile,** *Hydrocyanpararosaniline*, results upon digesting pararosaniline salts with alcohol and potassium cyanide. *Hydrocyanrosaniline* is similarly obtained from the rosaniline salts. The hydrochlorides of these hydrocyan-bodies break down under the influence of heat into HCl, HCN, and the salts of rosaniline.

B. **Sym. Diphenylethane Group: Dibenzyl,** sym. *Diphenylethane*, $C_6H_5.CH_2.CH_2.C_6H_5$, melting at 52° and boiling at 284°, is prepared (1) by the action of sodium or (copper) upon benzyl chloride, $C_6H_5.CH_2Cl$, or (2) of $AlCl_3$ upon benzene and ethylene chloride or ω-chlorethyl benzene (A. **235**, 155), and (3) by heating benzoïn,

stilbene, and tolane with hydriodic acid. It forms stilbene and tolane when heated to 500°. Chromic acid and potassium permanganate oxidize it directly to benzoic acid. It yields two dinitro-compounds by nitration.

p,p-**Dinitrodibenzyl** has also been obtained by the action of stannous chloride upon p-nitrobenzyl chloride. It melts at 179° (A. **238**, 272; B. **20**, 909).

Dibenzyl Homologues: *α,β*-**Phenyltolylpropane**, $C_6H_5CH(CH_3)CH_2C_6H_4CH_3$, and *α,β*-**Phenylxylylpropane**, are produced when concentrated sulphuric acid acts upon styrol in the presence of xylene or trimethylbenzene. The homologous benzenes, containing a methyl group, attach themselves to the unsaturated linkage in the styrol (B. **23**, 3269).

Diphenyldimethyl Ethane, $C_6H_5 . CH(CH_3)CH(CH_3)C_6H_5$, melting at 123°, is formed when sodium or zinc-dust acts upon a *β*-haloid ethylbenzene, $C_6H_5 . CHX . CH_3$ (B. **26**, 1710).

Stilbene, Toluylene, sym. *Diphenyl-ethylene*, $C_6H_5 . CH : CH . C_6H_5$, melting at 124° and boiling at 306°, crystallizes in large, glistening (*στίλβειν*, to glisten) monoclinic leaflets or prisms. It is obtained by a great variety of methods. It belongs to a long-known class of aromatic substances (Laurent, 1844). It is produced:

(1) By distilling benzyl sulphide and disulphide;

(2) By heating polymeric thiobenzaldehyde (p. 185) to 150°, or by distilling trithiobenzaldehyde with metallic copper (B. **25**, 600);

(3) By the action of metallic sodium upon benzaldehyde or benzal chloride;

(4) From chlorinated, asymmetrical diphenyl ethane derivatives—*e. g.*, $(C_6H_5)_2CH . CH_2Cl$ (p. 368), $(C_6H_5)_2CH . CCl_3$, by a rearrangement caused by heat or zinc-dust (B. **7**, 1409; J. pr. Ch. [2], **47**, 44);

(5) By the action of metallic copper, potassium sulphydrate (B. **24**, 1776), or potassium cyanide (B. **11**, 1219) upon stilbene dihalides.

(6) An interesting method for its production is that of distilling fumaric and cinnamic phenyl esters (B. **18**, 1945):

$$\underset{\text{Diphenyl Fumaric Ester}}{C_6H_5OCOCH{:}CH.COOC_6H_5} \xrightarrow{-CO_2} \underset{\text{Phenyl-cinnamic Ester}}{C_6H_5.CH : CH.CO.OC_6H_5} \xrightarrow{-CO_2} \underset{\text{Stilbene.}}{C_6H_5.CH : CH.C_6H_5}$$

When heated with hydriodic acid stilbene yields dibenzyl. The addition of halogens produces stilbene dihaloids, the haloid esters of the hydrobenzoïns (p. 371). Chromic acid oxidizes stilbene to benzaldehyde and benzoic acid. *Thionessal*, tetraphenylthiophene (see this), is produced when stilbene is heated for several hours at 250°, together with sulphur. Phenanthrene is formed when stilbene is heated.

Stilbenes having the substituents in the benzene nucleus are obtained from substituted benzyl- and benzal-chlorides; thus, o-chlorbenzal chloride and copper yield o,o-**Dichlorstilbene**, $(Cl . C_6H_4 . CH)_2$, melting at 97°, and chlornitrobenzyl chloride and alcoholic potash give rise to **Dichlornitrostilbene**, melting at 294° (B. **25**, 79; **26**, 640).

The action of alcoholic potash upon o- and p-nitrobenzyl chlorides gives rise to two physical isomerides in each case: two o,o-**Dinitrostilbenes**, melting at 126° and 196° respectively, and two p,p-**Dinitrostilbenes**, melting at 210–216° and 280–284° (B. **21**, 2072; **23**, 1959; **26**, 2232), which yield corresponding diamidostilbenes upon reduction. o_2-**Diamido-stilbene**, (cis-) melting at 123° and (trans-) at 168°, changes to *indol* (good yield) on heating equivalent quantities of the hydrochloride and base; aniline is eliminated (B. **28**, 1411). The disulphonic acid of p_2-**diamido-stilbene** (melting at 227°), by diazotizing and combining with phenol, passes into a tetrazo-compound, *brilliant yellow*. The mono-ethyl derivative,

$$\begin{array}{l} CH . C_6H_3(SO_3H)N : NC_6H_4OH \\ \| \\ CH . C_6H_3(SO_3H)N : NC_6H_4OC_2H_5 \end{array}$$

of the latter is the substantive cotton-dye, *chrysophenine* (B. **27**, 3357).

See B. 22, R. 311 (compare benzidine dyes, p. 338), for additional dye-substances. o,o-**Dioxystilbene**, melting at 92°, is produced, together with other bodies, on boiling salicylaldehyde with zinc-dust and glacial acetic acid (B. 24, 3175).

Tolane, *Diphenyl Acetylene*, $C_6H_5 . C : C . C_6H_5$, melting at 60°, is produced from stilbene bromide on boiling with alcoholic potash, and, further, together with diphenylvinyl ether (p. 368), on treating unsym. diphenylchlor-ethylene, $(C_6H_5)_2C : CHCl$, with sodium alcoholate.

The latter method proceeds more smoothly with the substituted tolanes. **Dimethyl Tolane,** melting at 136°, and **dimethoxytolane,** melting at 145°, are obtained from ditolyl- and dianisylchlorethylene. o,o-**Dichlortolane,** melting at 89°, is made from o,o-dichlorstilbene dichloride.

The tolanes absorb two and four halogen atoms, the products being tolane di- and tetra-chlorides (see these). The elements of water are taken up by the action of glacial acetic acid and sulphuric acid, with the formation of desoxybenzoïns (below) (compare vol. I, p. 96).

1. **Alcohol and Ketone Derivatives of Dibenzyl:**

$C_6H_5 . CH . OH$	C_6H_5CO	$C_6H_5 . CH . OH$	$C_6H_5 . CO$	C_6H_5CO
$C_6H_5 . CH_2$	$C_6H_5 . CH_2$	$C_6H_5 . CH . OH$	$C_6H_5 . CH . OH$	$C_6H_5 . CO$
Stilbene Hydrate	Desoxybenzoïn	Hydrobenzoïn	Benzoïn	Benzil.

Stilbene Hydrate, *Toluylene Hydrate*, $C_6H_5 . CH(OH) . CH_2 . C_6H_5$, melting at 62°, results upon reducing desoxybenzoïn with sodium amalgam.

Desoxybenzoïn, *Phenyl-benzyl ketone*, $C_6H_5 . CO . CH_2 . C_6H_5$, melting at 60° and boiling at 314°. It is obtained (1) by distilling a mixture of calcium benzoate and calcium α-toluate; (2) when $AlCl_3$ acts upon a mixture of alphatoluic chloride; (3) by reducing benzoïn with zinc and hydrochloric acid (B. 21, 1296); (4) from chlorobenzil and benzil (B. 26, R. 585) by the action of hydriodic acid; (5) by heating monobromtoluylene with water to 180-190°. One H-atom of its CH_2 group can be replaced by sodium and alkyls, but not the second (B. 21, 1297; 23, 2072). *Methyl-, isobutyl-, cetyl-desoxybenzoïn* melt at 58°, 78°, and 76° (B. 25, 2237).

Its *oxime* melts at 98°. *Isonitrosodesoxybenzoïn*, produced by N_2O_3, is identical with α-benzil monoxime (p. 373). Hydriodic acid converts desoxybenzoïn into dibenzyl—see also *stilbene hydrate*.

The nitration of desoxybenzoïn produces o-**nitrodesoxybenzoïn**, $C_6H_4(NO_2)CH_2 . CO . C_6H_5$, which, upon reduction, yields α-phenyl-indol, $C_6H_4\left\langle\begin{matrix}CH\\NH\end{matrix}\right\rangle C . C_6H_5$. **Desoxytoluoïn,** $CH_3 . C_6H_4 . CH_2 . CO . C_6H_4 . CH_3$, and **Desoxyanisoïn,** $CH_3O . C_6H_4 . CH_2 . CO . C_6H_4 . OCH_3$, are formed from the corresponding tolanes (A. 279, 335, 339) (above). $CSCl_2$, or carbon disulphide, and caustic potash, convert the desoxybenzoïns into *desaurines*, which form brilliant golden-yellow needles. They dissolve in sulphuric acid with a violet-blue color. The exact constitution of these bodies is not yet known. The simplest desaurine very probably has the composition $C_6H_5COC(CS)C_6H_5$ (B. 25, 1731, 2239).

Hydrobenzoïn, *Toluylene Glycol*, $C_6H_5 . CH(OH)CH(OH)C_6H_5$, has two asymmetric C-atoms and occurs in two optically inactive modifications (A. 259, 100): *hydrobenzoïn*, melting at 134°, and *isohydrobenzoïn*, melting at 119°. The latter has been resolved into two optically active components (see below). Both are produced, together with benzyl alcohol, when zinc and alcoholic hydrochloric acid act upon oil of almonds, or when the latter is treated with sodium amalgam, or in the electrolytic reduction of benzaldehyde (B. 29, R. 229). Both are also obtained from stilbene bromide or chloride on converting the latter by silver acetate or benzoate into esters, and saponifying these with alcoholic ammonia. With potassium acetate, isohydrobenzoïn is almost the sole product. Hydrobenzoïn predominates (with a little isohydrobenzoïn) when sodium amalgam acts on benzoïn. This is also the best method for its preparation (A. 248, 36).

Hydrobenzoïn dissolves with difficulty in water, crystallizes in rhombic plates, melting at 134°, and sublimes without decomposition. The *diacetate* is obtained from benzaldehyde and acetyl chloride by means of zinc-dust (B. **16**, 636): it melts at 134°.

Isohydrobenzoïn is more readily soluble in water. It crystallizes in prisms which contain water of crystallization and rapidly effloresce on exposure. Its *diacetate* is dimorphous, and crystallizes in shining leaflets, melting at 118°, or in rhombic prisms melting at 106°.

Dimolecular *anhydrides*, $\begin{array}{l} C_6H_5CH . O . CH . C_6H_5 \\ C_6H_5 . CH . O . CH . C_6H_5 \end{array}$ (?), melting at 132° and 102°, are obtained, together with diphenylacetaldehyde, $(C_6H_5)_2CH . CHO$, from both hydrobenzoïns by the action of sulphuric acid or P_2O_5.

By crystallization from ether isohydrobenzoïn has been resolved into enantiomorphous dextro- and lævo-rotatory crystals (B. **30**, 1531). Chromic acid or potassium permanganate changes both hydrobenzoïns into benzaldehydes, and nitric acid converts them into benzoïn (B. **24**, 1776). PBr_5 changes both to the same **stilbene dibromide,** $C_6H_5 . CHBr . CHBr . C_6H_5$, melting at 237°, which has also been made by the action of bromine upon stilbene and dibenzyl. Stilbene and bromine yield not only the body (the α-) melting at 237°, but also a β-variety, melting at 110°. This is more readily soluble. It passes into the higher-melting variety under the influence of heat, and this again reverts by alcoholic potash into *liquid* monobromstilbene, whereas the β-modification by similar treatment changes to a *solid* monobromstilbene (p. 375) (B. **28**, 2693). Both hydrobenzoïns are changed by PCl_5 into α- and β-**Stilbene Dichloride,** melting at 192° and 93°. The α-compound is also produced when chlorine acts upon stilbene dissolved in chloroform. When heated to 200° the β- passes into the α-variety.

Diphenyloxethylamine, $C_6H_5 . CH(OH)CH(NH_2)C_6H_5$, melting at 161°, and **isodiphenyloxethylamine,** melting at 128°, are produced together by the reduction of benzoïnoxime, and also from the condensation products of glycocoll with benzaldehyde, as well as from benzaldehyde and benzylamine by the action of sodium hydroxide. N_2O_3 converts isodiphenyloxyethylamine into isohydrobenzoïn (B. **28**, 1866, 2524; **29**, 295; **30**, 1527). **Diphenyl-ethylene-diamine,** *Stilbene Diamine*, $C_6H_5CH(NH_2)CH(NH_2)C_6H_5$, melting at 91°, is produced by reducing benzil dioxime with sodium and alcohol. It is resolved by crystallization of its bitartrate into two optically active components (B. **28**, 3167).

The *diesoanhydride* of an o,o-**dioxyhydrobenzoïn,** $O . C_6H_4 . CH . CH . C_6H_4O$, has been obtained in two modifications, melting at 68° and 114°, by the reduction of salicylaldehyde with zinc-dust and glacial acetic acid.

Benzoïn, *ω Benzyl Alcohol Phenyl Ketone*, melting at 134°, $C_6H_5 . CH(OH) . CO . C_6H_5$, is produced when the hydrobenzoïns are oxidized with concentrated nitric acid, and by the condensation of two molecules of benzaldehyde with potassium cyanide in aqueous-alcoholic solution.

This reaction is also shown by other aromatic aldehydes (see B. **25**, 293; **26**, 60). The products are ketone alcohols,—*e.g.*, *anisoïn*, $CH_3O . C_6H_4CH(OH)CO . C_6H_4 . OCH_3$; *Cuminoïn*, etc., from anisic aldehyde, cuminol (see also furfurol, phenylglyoxal),—and reduce Fehling's solution, being at the same time oxidized to the corresponding benzils.

Chromic acid oxidizes benzoïn to benzaldehyde and benzoïc acid, while nitric acid changes it to benzil; nascent hydrogen reduces it to hydrobenzoïn. The latter and benzil are produced when benzoïn is boiled with alcoholic potash. If air be simultaneously introduced, benzil is the chief product, and it is further changed to benzilic acid (p. 369).

Benzoïn Hydrazone melts at 75° (J. pr. Ch. [2], **52**, 124). The *phenylhydrazones* melt at 158° and 106° (B. **28**, R. 788). The *oxime* melts at 152°. Alcohols and hydrochloric acid alkylize benzoïn: *methyl benzoïn*, $C_6H_5CH(OCH_3)COC_6H_5$, melts at 50°, and *ethyl benzoïn* at 62° (B. **26**, 2412).

The hydrobromic acid ester of benzoïn—**desylbromide**, $C_6H_5 . CHBrCOC_6H_5$, melting at 55°—is obtained from desoxybenzoïn (see below) and bromine. Aniline converts it into **desylanilide**, *benzoïnanilide*, $C_6H_5CH(NHC_6H_5)CO . C_6H_5$, melting at 99°, which is also produced when aniline is heated together with benzoïn. When heated together with aniline hydrochloride to 160°, the product is **benzoïnanilanilide**, $C_6H_5CH(NH . C_6H_5)C(NC_6H_5)C_6H_5$, melting at 125°; and when with aniline and zinc chloride at still higher temperatures: *diphenylindol*, $\begin{matrix} NH\ .\ C_6H_4 \\ C_6H_5C = C . C_6H_5 \end{matrix}$ (B. **26**, 1336, 2640).

Benzoïn-p-toluide, $C_6H_5CH(NHC_6H_4 . CH_3)CO . C_6H_5$, melting at 145°, is formed in the condensation of benzaldehyde with benzylidene toluidine by means of potassium cyanide (B. **29**, 1736). o-Diamines and benzoïn condense to *dihydroquinoxalines*; urea and thioureas with benzoïn yield *glyoxalines*, while *oxazoles* are produced in the condensation of benzoïn with acid nitriles. For the condensation products of benzoïn with acetone and acetophenone consult B. **26**, 65, and p. 380.

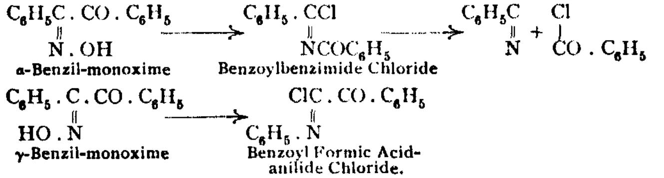
Benzil, Dibenzoyl, *Diphenylglyoxal*, $C_6H_5 . CO . CO . C_6H_5$, melting at 90° and boiling at 347°, consists of beautiful yellow prisms. It is the most easily obtained α-diketone. It is produced on boiling stilbene bromide with water and silver oxide and by digesting benzoïn with concentrated nitric acid.

Benzil and hydrazine hydrate form **hydrazibenzil**, $C_6H_5C\left(\left\langle\begin{matrix}NH\\|\\NH\end{matrix}\right\rangle\right)CO . C_6H_5$, and **bishydrazibenzil**, $\left[C_6H_5C\left(\left\langle\begin{matrix}NH\\|\\NH\end{matrix}\right\rangle\right)\right]_2$, which yield **azobenzil**, $C_6H_5C\left(\left\langle\begin{matrix}N\\ \| \\N\end{matrix}\right\rangle\right)CO.C_6H_5$ and **bisazobenzil**, $\left[C_6H_5 . C\left(\left\langle\begin{matrix}N\\ \| \\N\end{matrix}\right\rangle\right)\right]_2$, on oxidation (B. **29**, 775). The *osazone*, $(C_6H_5)_2 . C_2(NNH . C_6H_5)_2$, melting at 225°, becomes triphenylosotriazole on heating (A. **232**, 230; B. **26**, R. 198). An isomeric modification of benzilosazone, melting at 208°, has been obtained by the action of iodine and sodium ethylate upon benzalphenylhydrazone. When heated above its melting point it changes to the higher melting modification (B. **29**, R. 863).

One molecule of hydroxylamine, acting upon benzil, produces two isomeric **monoximes**, the α- melting at 134°, and the γ- at 113°.

The former passes into the latter by heating it to 100° with alcohol, or upon dissolving it in glacial acetic acid with hydrochloric acid. α-Monoxime and hydroxylamine form α-benzil dioxime, while the γ-monoxime yields γ-benzil dioxime (B. **22**, 540, 709). Compare B. **26**, 792, R. 52, for their behavior with phenylhydrazine.

Both monoximes break down, upon heating, into benzonitrile and benzoic acid. The deportment of the benzil monoximes in the Beckmann oxime rearrangement is very interesting. It is effected by means of PCl_5: α-monoxime yields benzoyl benzimide chloride, readily decomposing into benzonitrile and benzoyl chloride, while the γ-monoxime yields benzoylformic acid-anilide chloride:



In the first instance the hydroxyl exchanged positions with the phenyl residue, in the second with the benzoyl residue, which led to the above accepted configuration of the monoximes.

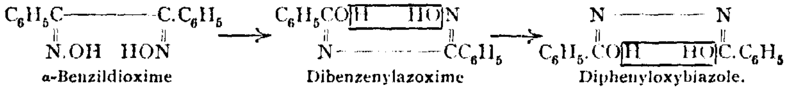
Two molecules of hydroxylamine convert benzil into two isomeric benzil dioximes.

the α- melting at 237° and the β- at 207°. A third γ-benzil dioxime has been prepared from γ-benzil monoxime; it melts at 163°. The β-dioxime is the most stable; the other modifications rapidly change to it. Under certain conditions the γ-dioxime rearranges itself into the α-form (A. **274**, 33).

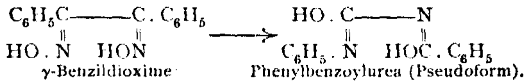
Three different esters are produced with acid anhydrides: *benzil-dioxime diacetates*—the α-form melting at 148°, the β- at 124°, and the γ- at 114°. Sodium hydroxide saponifies the α- and β-diacetates to their oximes, while the γ-acetate yields the *anhydride*, $\begin{array}{l}C_6H_5C:N\\ \quad\;\, | \\ C_6H_5C:N\end{array}\!\!>O$, *diphenylfurazane* (see this), which also results from all three dioximes by the exit of water. Potassium ferricyanide, in alkaline solution, oxidizes all three to the *peroxide*, $\begin{array}{l}C_6H_5C=N-O\\ \quad\;\, | \qquad\quad\;\; | \\ C_6H_5C=N-O\end{array}$, melting at 114°. This, when rapidly distilled, breaks down into two molecules of phenylcyanate.

A complete picture is also afforded by the deportment of the three dioximes in the Beckmann rearrangement, which has led to a formula for the present case of isomerism on the assumption that the oxime hydroxyls invariably exchange positions with the atomic groups adjacent to them (A. **274**, 1):

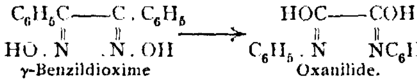
I. α-Benzildioxime yields chlorides with PCl_5 by a change in position first of the one and then of the second hydroxyl, which can be converted into the anhydrides: *dibenzenylazoxime* (see this) and *diphenyloxybiazole* (see this), whose hydrates are included in the following diagram for the sake of clearness:



II. γ-Benzildioxime in the first stage of the reaction also yields dibenzenylazoxime, but by a second change in position *phenylbenzoyl urea* is produced:



III. β-Dioxime by a double change in position yields *oxanilide*:



The ready transition of the γ-diacetate into furazane is not in harmony with the preceding configuration of the dioximes; this might rather be expected from the α-diacetate.

The analogy of the benzil dioximes with the osazones of dioxosuccinic ester is rather remarkable (I, 528). These osazones also occur in three forms, one of which is the stable and the other two unstable, so that the assumption of similar causes for the isomerism is not yet excluded (B. **28**, 64).

Aniline and benzil heated to 200° yield *benzil monanil*, $C_6H_5CO.C(NC_6H_5)C_6H_5$, melting at 106°; on adding P_2O_5 the product is *benzil dianil*, $C_6H_5C(NC_6H_5)C(NC_6H_5)$-$C_6H_5$, melting at 142° (B. **25**, 2600; **26**, R. 700). Benzil, being an o-diketone, is particularly well adapted for the formation of heterocyclic rings. It condenses with ethylene diamine to a *dihydropyrazine* derivative, with ortho-diamines to *quinoxalines*, with o-amido-diphenylamine to a *stilbazonium base* (see this), with ureas and thioureas to *ureïnes* and *diureïnes*, with semicarbazide to *oxydiphenyltriazine*, etc. Hydriodic acid reduces it to desoxybenzoïn, while chromic acid oxidizes it to benzoic acid. On standing with potassium cyanide and alcohol it breaks down into benzoic acid and benzaldehyde. See B. **28**, R. 465; **29**, R. 645, 865; C., 1897, I, 596, for the condensation of benzil with malonic ester and acetoacetic ester.

The conversion of benzil into benzilic acid (p. 369) by fusion with caustic potash or upon boiling with alcoholic potash is important:

$$C_6H_5 . CO . CO . C_6H_5 \xrightarrow{H_2O} (C_6H_5)_2C(OH)COOH.$$

Phosphorus pentachloride changes benzil to **chlorobenzil**, $C_6H_5 . COCCl_2C_6H_5$, melting at 61°, and later to **tolane tetrachloride**, $C_6H_5CCl_2CCl_2C_6H_5$, melting at 163°. The latter has also been obtained synthetically on heating benzotrichloride with copper, whereas benzil is produced when it is heated together with glacial acetic acid or sulphuric acid.

As benzil is obtained from benzoïn, so **anisil**, $(CH_3O . C_6H_4CO)_2$, melting at 133°, **cuminil**, $(C_3H_7 . C_6H_4CO)_2$, melting at 84°, have been prepared by the action of nitric acid upon anisoïn and cuminoïn (p. 372). Anisil and a **hexamethoxybenzil**, $[(CH_3O)_3C_6H_2CO]_2$, melting at 189°, have been obtained by alkaline reducing agents from anisamide and trimethylgallamide (B. 24, R. 523).

These benzils, when fused with caustic potash, yield:

Anisilic Acid, *Cumilic Acid*, and *Hexamethoxybenzilic Acid* (p. 369).

2. **Alcohol Derivatives of Stilbene** are not known in a free condition; when their esters are saponified, isomeric ketones are obtained for the most part (see phenylvinyl alcohols, p. 271):

Bromstilbene $C_6H_5CBr:CH.C_6H_5 \xrightarrow{H_2O} C_6H_5.CO.CH_2.C_6H_5$ Desoxybenzoïn.

Isobenzil $C_6H_5C(OCOC_6H_5):C(OCOC_6H_5)C_6H_5 \rightarrow C_6H_5CO.CH(OH).C_6H_5$ Benzoïn.

However, benzoïn reacts in most cases as if it were an unsaturated glycol with the formula $C_6H_5C(OH):C(OH)C_6H_5$.

Monochlorstilbene, $C_6H_5CH : CCl . C_6H_5$, is an oil, boiling at 320-324°. It is produced when PCl_5 acts upon desoxybenzoïn, and by the action of alcoholic potash on stilbene dichloride. When boiled with glacial acetic acid it is transformed into an isomeric modification, melting at 54°. Chlorine and bromine convert it into **chlorstilbene dichloride**, $C_6H_5CCl_2 . CHCl . C_6H_5$, melting at 103°, and **chlorstilbene dibromide**, melting at 127° (C., 1897, 1, 858). **Methyl chlorstilbene**, $C_6H_5C(CH_3) : CClC_6H_5$, is obtained from methyldesoxybenzoïn and deports itself similarly. It is an oil, and melts at 118° (B. 25, 2237; 29, R. 34). **Monobromstilbene**, melting at 31°, results on treating stilbene dibromide, melting at 110°, with alcoholic potash; whereas the stilbene dibromide, melting at 237°, yields a liquid bromstilbene. On the application of heat the oil passes into the solid isomeride; the latter, by further action of caustic potash, changes more readily to tolane than the liquid isomeride. Therefore, this probably has the *syn*-configuration (B. 28, 2700).

Isobenzil, *Stilbene-glycol Dibenzoate*, $C_6H_5C(O . COC_6H_5) : C(OCOC_6H_5)C_6H_5$, colorless needles, melting at 156°, is obtained by the action of metallic sodium upon the ethereal solution of benzoyl chloride (compare 1, 297). It is a polymeride of benzil. When saponified with caustic potash it is resolved into benzoic acid and benzoïn (B. 24, 1264).

Dichlorstilbene, *Tolane Dichloride*, $C_6H_5CCl : CCl . C_6H_5$, exists in two modifications: α-, melting at 143°, and the β- at 63°. Both are formed by the addition of chlorine to tolane, or by the reduction of tolane tetrachloride with iron and acetic acid, as well as from chlorstilbene dichloride (see above) with caustic potash. **Chlorbromstilbene**, $C_6H_5CCl : CBrC_6H_5$, melting at 174°, is similarly prepared from chlorstilbene dibromide. **Dibromstilbenes**, α- melting at 208° and β- melting at 64°, are obtained from tolane and bromine. **Tolallyl Sulphide**, *Tolane Sulphide*,

$$\begin{array}{c} C_6H_5C : CC_6H_5 \\ \diagdown\ \diagup \\ S \end{array}$$

, melting at 174°, is very probably the anhydride of a thiostilbene glycol. It is formed, together with stilbene, on heating benzyl sulphide (B. 24, 3313).

3. **Carboxylic Acids of the Dibenzyl Group** are (a) those in which the carboxyl group is in the benzene nucleus; (b) such as have the carboxyl group in the side-chain: diphenylated fatty acids.

The first group is composed chiefly of a series of o-carboxylic acids produced by phthalic anhydride condensations:

(a) o-**Desoxybenzoïn Carboxylic Acid,** $C_6H_5.CH_2.CO.C_6H_4.COOH(+H_2O)$, melting at 75°, is formed when boiling alkalies act on the corresponding lactone. **Benzylidene Phthalide,** *Benzal Phthalide*, $C_6H_4.CH:\overline{CC_6H_4COO}$, melting at 99°, which results from the condensation of phthalic anhydride and phenylacetic acid with the elimination of CO_2.

By means of nitrobenzalphthalide, benzalphthalide can be changed to **isobenzalphthalide,** $C_6H_5\overline{C:CH.C_6H_4.COO}$, melting at 91°, the anhydride of β,o **desoxybenzoïn carboxylic acid,** $C_6H_5.CO.CH_2.C_6H_4.CO_2H$, melting at 163°. The latter is made by decomposing β-phenylhydrindone (p. 387) with caustic soda. Benzalphthalide sustains a different rearrangement under the influence of sodium alcoholate; the sodium salt of β-phenyldiketohydrindene (p. 388) is then produced:

$$C_6H_5.\overline{C:CH.C_6H_4.COO} \leftarrow C_6H_5CH:\overline{C.C_6H_4.COO} \rightarrow C_6H_4\overline{CH.CO.C_6H_4.COO}$$

Isobenzalphthalide — Benzalphthalide — Phenyldiketohydrindene.

Hydrazine converts benzalphthalide into **benzylphthalazone,** $C_6H_5.CH_2.\overset{\|}{C}.C_6H_4.CO$ (with N——NH bridging). By reduction with glacial acetic acid and zinc it passes into **benzylphthalimidine,** $C_6H_5CH_2.\overline{CHC_6H_4.CO.NH}$, melting at 137°. It can also be obtained by the reduction of benzalphthalimidine (B. **29**, 1434, 2743).

o,o-**Desoxybenzoïn Dicarboxylic Acid,** $COOH.C_6H_4.CH_2.CO.C_6H_4.COOH$, melting at 239°, is obtained upon heating phthalic anhydride with o-carbophenylacetic acid and sodium acetate (B. **24**, 2820). The reduction of desoxybenzoïn-mono- and -dicarboxylic acids yields **dibenzyl mono- and di- carboxylic acids,** melting at 131° and 225°. The oxidation of o-desoxybenzoïn carboxylic acid produces o-**benzil-carboxylic acid,** $C_6H_5.CO.CO.C_6H_4.COOH$, occurring in two modifications, one *yellow* in color, melting at 141°, and another *white*, melting at 125-130° (B. **23**, 1344, 2079; **29**, 2745).

o,o-**Benzil Dicarboxylic Acid,** $(COOH.C_6H_4.CO)_2$, is white and melts at 270°. It forms two series of dialkyl esters—white and yellow in color respectively. The acid is formed from phthalic anhydride with zinc-dust and acetic acid and subsequent oxidation, or by the oxidation of **Diphthalyl,** $\overline{O.OC.C_6H_4C}:\overline{CC_6H_4COO}$, melting at 234°. This latter body has been produced by the condensation of phthalide (p. 234) and phthalic anhydride with potassium cyanide (see formation of benzoïn, p. 372). **Tetramethoxydiphthalyl,** $\overline{O.OC.C_6H_2(OCH_3)_2C}:\overline{CC_6H_2(OCH_3)COO}$ (B. **24**, R. 820; compare B. **26**, 540), is similarly made by the condensation of opianic ester. **Dihydrodiphthalyldiimide,** $\overline{NH.CO.C_6H_4.CH}.\overline{CHC_6H_4CO.NH}$, melting with decomposition at 284°, results from the condensation of two molecules of phthalic anhydride with methyl alcoholic ammonia. This substance is isomeric with indigo white (compare B. **29**, 2745).

(b) **Dibenzyl Carboxylic Acid,** *a-Phenylhydrocinnamic Acid, a,β-Diphenyl-propionic Acid*, $C_6H_5CH_2CH(C_6H_5)COOH$, appears in three physical isomerides, melting at 95°, 89°, 82°, boiling at 335° (B. **25**, 2017). Its *nitrile* results upon introducing benzyl into benzyl cyanide. a-**Phenyl-o-amidohydrocinnamic Acid,** melting at 148°, is obtained in the reduction of a-phenyl-o-nitrocinnamic acid (B. **28**, R. 391). It changes very readily into its lactone—*β-phenylhydrocarbostyril*, $C_6H_4\begin{matrix}\diagup CH_2—CH(C_6H_5)CO \\ \diagdown NH———————\end{matrix}$, melting at 174°.

Stilbene Carboxylic Acid, *a-Phenylcinnamic Acid*, $C_6H_5CH:C(C_6H_5)CO_2H$, melting at 172°, is formed in the condensation of benzaldehyde with phenylacetic acid.

By reduction it becomes α-phenylhydrocinnamic acid, but does not add bromine. The action of bromine upon the sodium salt produces bromstilbene (B. **26**, 659). α-**Phenyl-o-amido-cinnamic Acid,** melting at 186°, the reduction product of o-nitro-α-phenylcinnamic acid, obtained in the condensation of o-nitrobenzaldehyde with phenylacetic acid, yields β-phenanthrene carboxylic acid (see this) (B. **29**, 496) when its diazo-derivative is shaken with copper in powder form.

Desylacetic Acid, *β-Phenylbenzoyl Propionic Acid*, $C_6H_5.COCH(C_6H_5).CH_2.COOH$, melting at 161°, is obtained as ester from the interaction of sodium desoxybenzoïn and chloracetic ester. When distilled in vacuum it changes to **diphenylcrotolactone,** $C_6H_5C:C(C_6H_5)CH_2COO$ (ring), melting at 151° (B. **25**, R. 419). See B. **29**, 2585, for the formation of desylacetic acid from the condensation product of benzaldehyde with phenylpyroracemic acid.

Dibenzyl-dicarboxylic Acid, sym. **Diphenyl-succinic Acid,**

$$\begin{array}{l} C_6H_5.CH.COOH \\ \quad\;\; | \\ C_6H_5.CH.COOH \end{array},$$

occurs similarly to the dialkyl succinic acids in two isomeric forms. The *α-acid* (+ H_2O) is produced on heating phenyl-bromacetic acid (2 mols.) with alcoholic CNK, also (*together with the β-acid, melting at 229°*) *from stilbene dicarboxylic* acid with sodium amalgam. The acid, containing one molecule of water, melts at 185° when rapidly heated; it loses water and remelts at 220°. When heated to 200° with hydrochloric acid it changes to the β-acid. Its *anhydride*, melting at 116°, is readily produced by means of acetyl chloride.

The β-acid yields an *anhydride* (but with more difficulty) when heated with acetyl chloride (B. **23**, 117, R. 574; A. **259**, 61). It melts at 112°.

The *nitriles*, $C_6H_5CH(CN)CH(CN)C_6H_5$, the α- melting at 160° and the β- melting at 240°, result from the condensation of phenyl-acetonitrile with mandelo-nitrile by means of potassium cyanide (B. **25**, 289; **26**, 60). Both nitriles yield the β-acid when they are saponified.

Stilbene Dicarboxylic Acid, Diphenyl Maleïc Acid, decomposes immediately when separated from its salts, like the dialkylic maleïc acids, into water and its *anhydride*,

$$\begin{array}{l} C_6H_5.C.CO \\ \quad\;\; \| \qquad\; >O \\ C_6H_5.C.CO \end{array},$$

melting at 155°. The latter condenses, like phthalic anhydride, with phenylacetic acid and quickly changes to **benzaldiphenylmaleïd,**

$$\begin{array}{l} C_6H_5C - C{=}CH.C_6H_5 \\ \quad\;\; \| \qquad\qquad >O \\ C_6H_5C - CO \end{array},$$

which deports itself just like benzalphthalide (p. 376) (B. **24**, 3854). The salts of diphenylmaleïc acid are formed when **dicyanstilbene,** $C_6H_5C(CN):C(CN)C_6H_5$, melting at 158°, are saponified with alcoholic potash. This nitrile is produced when phenylchloracetonitrile is treated with CNK or $NaOC_2H_5$, or by the action of sodium alcoholate and iodine upon phenylacetonitrile (B. **25**, 285, 1680).

4,5-Diphenyloctan-2,7-dion,

$$\begin{array}{l} C_6H_5.CH.CH_2.CO.CH_3 \\ \qquad\quad | \\ C_6H_5.CH.CH_2.CO.CH_3 \end{array},$$

melting at 161° and boiling at 335–340°, may be regarded as a derivative of dibenzyl. It might be designated *α,β-diacetonyl-dibenzyl*. It results in the reduction of 2 molecules of benzylidene acetone in feebly acid or neutral solution (B. **29**, 380, 2121).

C. Tri- and Tetra-phenyl Ethane Group.

A triphenyl ethane, $(C_6H_5)_2CH.CH_2.C_6H_5$, is not known (see C., 1897, I, 1204).

Triphenyl Ethanon, or *Triphenylvinyl Alcohol*, $(C_6H_5)_2.CH.CO.C_6H_5$, or $(C_6H_5)_2C:C(OH)C_6H_5$, melting at 136°, results from the action of benzene and aluminium chloride upon chloral, upon dichlor- or trichloracetyl chloride (B. **29**, R. 292; A. **296**, 219). Potassium permanganate oxidizes it to benzophenone and benzoic acid, while alcoholic potash resolves *it into diphenylmethane and benzoic acid. Bromine in* carbon disulphide converts it into **Triphenyl-bromethanon,** $(C_6H_5)_2CBrCOC_6H_5$, melting at 97°, in glacial acetic acid, however, by replacement of bromine with hydroxyl *triphenyloxyethanon* results. It does not react with phenylhydrazine. With hydroxylamine hydrochloride in alcoholic solution, oxidation takes place and **triphenylethoxyethanon,** $(C_6H_5)_2C(OC_2H_5)COC_6H_5$, is produced. Caustic potash breaks this body down into benzhydrol-ether and benzoic acid.

Triphenylmethyl Ethane, *α,α,β-Triphenylpropane*, $(C_6H_5)_2CH \cdot CH(CH_3)C_6H_5$, is probably the product obtained by the reduction of diphenylindone (p. 386) with phosphorus and hydriodic acid. Diphenylindone is an intermediate product in the condensation of benzophenone chloride with phenylacetic ester, whereby there results—

Triphenyl Acrylic Ester, $(C_6H_5)_2C : C(C_6H_5)COOR$. The acid, melting at 213°, corresponding to this ester is obtained from its *nitrile*, melting at 163°, the condensation product of benzophenone chloride and benzyl cyanide (B. **28**, 2784; **29**, 2841). When diphenylindone is fused with caustic potash it yields an acid, melting at 186°, which is isomeric with triphenyl acrylic acid. It is probably—

α,β-**Diphenylvinyl-o-benzoic Acid,** $COOH[2]C_6H_4C(C_6H_5) : CH \cdot C_6H_5$. Both acids, when heated with $ZnCl_2$, revert again to diphenylindone (B. **30**, 1282).

Tetraphenyl Ethane, $(C_6H_5)_2CH \cdot CH(C_6H_5)_2$, melting at 209° and boiling at 379–383°, is formed when benzophenone (p. 345) or benzohydrol chloride, $(C_6H_5)_2CHCl$ (p. 344), is heated with zinc, and thiobenzophenone (p. 346) with copper; further, by the reduction of tetraphenylethylene with sodium and alcohol, of benzpinacone or benzpinacoline (see below) with hydriodic acid and phosphorus, as well as by the condensation of stilbene bromide, of tetrabromethane, or of chloral with benzene and Al_2Cl_6 (B. **18**, 657; **26**, 1952; A. **296**, 221).

Tetraphenyl Ethylene, $(C_6H_5)_2C : C(C_6H_5)_2$, melting at 221°, is formed, together with tetraphenyl ethane, from benzophenone, and is also obtained on heating benzophenone chloride with silver or with zinc-dust, together with the benzpinacolines (B. **29**, 1789). Both hydrocarbons are split into two molecules of benzophenone when oxidized.

The *alcohols* of the tetraphenyl group are the pinacones of benzophenone and its homologues. They are formed, like the pinacones of the aliphatic series, from the ketones, together with secondary alcohols, by the action of nascent hydrogen.

Benzpinacone, *Tetraphenylethylene Glycol*, $(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2$, melts at 185° and splits into benzophenone and benzhydrol. It sustains a like change when boiled with alcoholic potash. It is formed from benzophenone by the action of zinc and sulphuric acid or by the decomposition of sodium benzophenone (B. **25**, R. **15**).

On heating benzpinacone with hydrochloric or dilute sulphuric acid to 200°, by the action of methyl chloride upon it, or of zinc-dust and acetyl chloride upon benzophenone, we get two

Benzpinacolines—the *α*-, melting at 205°; the *β*- variety, at 179°. So far as their structure is concerned, they are imperfectly known (B. **24**, R. 664).

Tetraphenylethane Dicarboxylic Acid, Tetraphenyl Succinic Acid,
$$\begin{array}{l}(C_6H_5)_2C \cdot COOH \\ \quad | \\ (C_6H_5)_2C \cdot COOH\end{array}$$
melting at 261° with decomposition (its *ethyl ester* at 89°), is obtained from diphenyl chloracetic ester by the action of silver (B. **22**, 1538). Its *nitrile*, melting at 215°, is formed by the interaction of the nitrile of diphenylacetic acid with sodium and iodine.

The dilactone of a **Benzpinacone-o₂-dicarboxylic Acid,** $O \cdot CO \cdot C_6H_4C(C_6H_5) \cdot C(C_6H_5)C_6H_4COO$, melting at 265°, is formed on boiling o-benzoylbenzoic acid (p. 350) with hydriodic acid and phosphorus (B. **29**, R. 498).

V. *ω,ω*-**Diphenylpropane Group: Dibenzylmethane,** *α,γ-Diphenylpropane*, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, boiling at 290–300°, results by the reducing action of hydriodic acid upon **Dibenzyl Ketone,** $C_6H_5 \cdot CH_2 \cdot CO \cdot CH_2 \cdot C_6H_5$, melting at 40° and boiling at 330° (B **24**, R. 946). This body is produced in the distillation of calcium phenylacetate. *One* hydrogen atom of each of the two CH_2-groups can be replaced by alkyls. It condenses with oxalic ester and sodium ethylate to a *Triketo*-R-*pentene* derivative, oxalyldibenzylketone (compare p. 20 and B. **27**, 1353; A. **284**, 245):

$$CO\begin{cases}CH_2 \cdot C_6H_5 \\ CH_2 \cdot C_6H_5\end{cases} + \begin{array}{l}COOH \\ | \\ COOH\end{array} \longrightarrow CO\begin{cases}CH(C_6H_5)-CO \\ \quad\quad\quad\quad\quad | \\ CH(C_6H_5)-CO\end{cases}$$

Sodium reduces dibenzylketone to **dibenzylcarbinol,** $(C_6H_5 \cdot CH_2)_2CH \cdot OH$, boiling at 327°. It combines to *dibenzyldiphenol methane*, $(C_6H_5CH_2)_2C(C_6H_4OH)_2$ (B. **25**,

1271), with phenol. **Benzylacetophenone,** $C_6H_5CH_2 . CH_2 . CO . C_6H_5$ m. p. 73°, is isomeric with dibenzylketone. It is produced on reducing **benzylidene acetophenone,** $C_6H_5CH : CH . CO . C_6H_5$ (m. p. 58°, b. p. 346°), with zinc-dust and acetic acid. This latter compound is the condensation-product of benzaldehyde and acetophenone (B. **20,** 657). It combines with hydrochloric acid to **chlorbenzylacetophenone :**

$$\underset{\text{Chlorbenzylacetophenone}}{C_6H_5.CHCl.CH_2.CO.C_6H_5} \xleftarrow{HCl} C_6H_5CH{:}CH.CO.C_6H_5 \xrightarrow{H_2} \underset{\text{Benzylacetophenone.}}{C_6H_5CH_2.CH_2.CO.C_6H_5}$$

o-, m-, p **Oxybenzylideneacetophenone,** from the corresponding oxybenzaldehydes and acetophenone, *melt at* 154° *with decomposition, at* 160°, *and* 183°. Alcoholic potash converts acetyl-o-oxybenzylideneacetophenone into *benzoylcumarone* (see this),

$$C_6H_4\left\langle\begin{matrix} O- \\ CH \end{matrix}\right\rangle C . CO . C_6H_5.$$

Reduction changes o-oxybenzylidene acetophenone into *a*-**phenyl** *γ*-(o-**oxyphenyl)propyl alcohol,** $HO . C_6H_4 . CH_2 . CH_2 . CH(OH)\text{-}C_6H_5$, melting at 97°, which is condensed by HCl in methyl alcohol to *a-phenylcumaran,*

$$C_6H_4\left\langle\begin{matrix} CH_2 . CH_2 \\ O \text{——} CH . C_6H_5 \end{matrix}\right. \quad (B.\ \mathbf{29},\ 244,\ 375).$$

The condensation of 2 mols. of acetophenone by heat alone, or by zinc ethide or zinc chloride, yields a homologue of benzalacetophenone, called **Dypnone,** $C_6H_5 . C(CH_3) : CH . CO . C_6H_5$, melting at 225° (22 mm.), which sustains the same relation to acetophenone as mesityl oxide bears to acetone (B. **27,** R. 339); see also triphenyl benzene (p. 342).

Benzaldehyde condenses as readily as acetophenone with desoxybenzoïn (p. 371), under the influence of alkalies, forming **benzylidenedesoxybenzoïn,** $C_6H_5CH : C(C_6H_5)CO . C_6H_5$, melting at 101°. This also results in the distillation of benzamarone (p. 383), and upon reduction yields **benzyldesoxybenzoïn,** $C_6H_5 . CH_2 . CH(C_6H_5)CO . C_6H_5$, melting at 120°. This can also be prepared by the introduction of the benzyl group into desoxybenzoïn (see p. 371). If benzaldehyde and desoxybenzoïn be condensed through the agency of hydrochloric acid, there is formed : **chlorbenzyldesoxybenzoïn,** which alkalies readily convert into the unsaturated ketone, while by distillation it is resolved into stilbene and benzoyl chloride (B. **26,** 447, 818) :

$$\begin{matrix} C_6H_5 . CH \\ \| \\ C_6H_5 . CCOC_6H_5 \end{matrix} \longleftarrow \underset{\text{Chlorbenzyldesoxybenzoïn.}}{\begin{matrix} C_6H_5 . CHCl \\ | \\ C_6H_5 . CH . CO . C_6H_5 \end{matrix}} \longrightarrow \begin{matrix} C_6H_5\ CH \\ \| \\ C_6H_5 . CH \end{matrix} + \begin{matrix} Cl \\ | \\ COC_6H_5. \end{matrix}$$

Dibenzoyl Methane, $(C_6H_5CO)_2CH_2$, is formed from dibenzoyl acetic acid. It melts at 81°. Nitrous acid converts it into an *isonitroso derivative,* $(C_6H_5 . CO)_2C : N . OH$, which may be converted into the corresponding

Diphenyl Triketone, $C_6H_5 . CO . CO . CO . C_6H_5$, boiling at 289° (175 mm. pressure) It solidifies to a golden-yellow mass, melting at 70°. It combines with water to a colorless hydrate (B. **23,** 3378).

Dibenzoylacetylmethane, *Dibenzoylacetone,* occurs in two forms, one of which probably represents the *diketohydroxyl form,* $(C_6H_5 . CO)_2C : C(OH)CH_3$ (*a*-, m. p. 80°), the other the *triketo form,* $(C_6H_5CO)_2 . CH . COCH_3$ (*β*-, m. p. 107–110°). It results from benzoyl acetone and benzoyl chloride with soda. Similarly, dibenzoylmethane yields (*β*)-**Tribenzoylmethane,** $(C_6H_5CO)_3CH$, melting at 225°. By boiling with potashes and acetic ester this *β*-modification is changed to the *a*-form, $(C_6H_5CO)_2C : C(OH)C_6H_5$, soluble in alkalies (A. **291,** 25).

Carboxylic Acids : **Dibenzyl Acetic Acid,** $(C_6H_5 . CH_2)_2CH . COOH$, melting at 87°, is derived from **dibenzyl malonic acid,** $(C_6H_5CH_2)_2C(COOH)_2$, the *ester* of which is produced by benzylating malonic ester. o,o-**Dinitrobenzyl Acetic Acid,**

$$C_6H_4\left\langle\begin{matrix} CH_2 - CH \text{——} CH_2 \\ NO_2 \quad\ COOH \quad NO_2 \end{matrix}\right\rangle C_6H_4,$$

made in an analogous manner, may be condensed by reduction with zinc-dust to *tetrahydronaphtinolin* (see this) (B. **27,** 2248; **29,** 636).

Dibenzoyl Malonitrile, $(C_6H_5CH_2)C(CN)_2$, melting at 130° and boiling at 360°, is obtained from the corresponding nitrilo-acid amide, which is prepared from cyanacet-

amide. Sodium and alcohol reduce the nitrile with elimination of a cyanogen group to **dibenzylethylamine**, $(C_6H_5CH_2)_2CH.CH_2.NH_2$, whose *hydrochloride* melts at 190° (B. 29, R. 1111).

Dibenzyl Glycollic Acid, $(C_6H_5.CH_2)_2C(OH).CO_2H$, **Oxatolylic Acid**, is produced from dibenzyl ketone by means of CNK and hydrochloric acid, and when vulpic and pulvic acids are boiled with dilute alkalies. It melts at 156°. When boiled with concentrated potassium hydroxide it decomposes into oxalic acid and two molecules of toluene (A. 219, 41).

a-Phenyl-β-benzoylpropionic Acid, *Phenylphenacyl Acetic Acid*, $C_6H_5CO.CH_2.$-$CH(C_6H_5)COOH$, melts at 153°. Its *nitrile* melts at 127°. The acid is produced when CNK acts upon chlorbenzylacetophenone (p. 379). If heated with acetic anhydride it yields the *lactone* of isomeric α,γ-**Diphenyl-γ-oxycrotonic Acid**, $C_6H_5C:CH.CH(C_6H_5)COO$, melting at 110°, while upon reduction with sodium amalgam, **α,γ-Diphenylbutyrolactone**, $C_6H_5.CH.CH_2.CH(C_6H_5)COO$ (A. 284, 1).

α,γ-**Diphenylacetoacetic Acid** is isomeric with phenylphenacylacetic acid. Its *ester*, $C_6H_5.CH_2.CO.CH(C_6H_5)CO_2C_2H_5$, melting at 79°, is formed when two molecules of phenylacetic ester are condensed with sodium ethylate. Concentrated sulphuric acid condenses the ester to a naphthalene derivative—phenylnaphthoresorcinol (A. 296, 1).

Dibenzoyl Acetic Acid, $(C_6H_5.CO)_2CH.COOH$, melts at 109°. Its *ester*, from benzoyl acetic ester and benzoyl chloride, yields CO_2 and dibenzyl methane by dry distillation, and acetophenone, carbon dioxide, and benzoic acid when digested with sulphuric acid.

VI. ω,ω-DIPHENYL BUTANE GROUP.

Dibenzyl Ethane, *α,δ*-**Diphenylbutane**, $C_6H_5.CH_2.CH_2.CH_2.CH_2.C_6H_5$, melting at 52°, is formed by the reduction of **Diphenylbutylene**, $C_6H_5.CH:CH.$-$CH_2.CH_2.C_6H_5$, which is produced when sodium and alcohol act upon the nitrile of α-phenylcinnamenyl acrylic acid (B. 23, 2857). **Diphenyldiethylene**, $C_6H_5.CH:$-$CH.CH:CH.C_6H_5$, melting at 148° and boiling at 250°, results on heating α-phenylcinnamenyl acrylic acid (B. 23, R. 333). A *tetra-iodide* of this hydrocarbon, $C_6H_5CI:$-$CI.CI:CIC_6H_5$, melting at 144° (B. 26, R. 19), is formed by the addition of iodine to

Diphenyl Diacetylene, $C_6H_5C:C.C:C.C_6H_5$, melting at 88°. This is made by shaking copper phenyl acetylide, $C_6H_5C:C.Cu$ (p. 268), in ammoniacal solution with air, or by the action of potassium ferricyanide. *It is the parent hydrocarbon of indigo blue.* Its o,o-*dinitro-derivative*, $C_6H_4<^{C:C.C:C}_{NO_2\quad O_2N}>C_6H_4$ (from o-nitro phenyl acetylene, p. 268), is rearranged by concentrated sulphuric acid into the isomeric di-isatogen (see this), which becomes indigo blue: $C_6H_4<^{CO}_{NH}>C:C<^{CO}_{NH}>C_6H_4$, by reduction with ammonium sulphide (B. 15, 53).

Ketones: **Phenethyl Benzyl Ketone**, $C_6H_5.CH_2.CH_2.CO.CH_2.C_6H_5$, boiling at 324° to 336°, is produced when hydrocornicularic acid is distilled with lime (p. 382).

Diphenacyl, *Dibenzoyl Ethane*, $C_6H_5CO.CH_2.CH_2.CO.C_6H_5$, melting at 145°, is made from phenacyl benzoylacetic ester (p. 371), as well as by the reduction of the two **bromdiphenacylens**, melting at 129° and 161°, with magnesium powder. These bromides are produced when sodium ethylate acts upon phenacyl bromide (B. 29, 1750, 2092). Being a γ-diketone, it readily forms *diphenylfurfurane*, *diphenylthiophene*, and *diphenylpyrrol*.

Desylacetophenone, *α,β-Dibenzoyl Phenyl Ethane*, $C_6H_5CO.CH(C_6H_5).CH_2.$-$COC_6H_5$, melting at 126°, is produced in the condensation of benzoïn and acetophenone with potassium cyanide (B. 23, R. 636; 26, 60). See B. 29, R. 171, for the action of hydrazine.

Bidesyl, $\begin{matrix} C_6H_5 . COCH . C_6H_5 \\ | \\ C_6H_5 . CO . CH . C_6H_5 \end{matrix}$, *dibenzoyl-dibenzyl*, results when desylbromide or iodine acts upon sodium desoxybenzoïn (B. **21**, 1355; **25**, 285). It melts at 255°. *Iso-bidesyl*, formed simultaneously, melts at 161°. Bidesyl yields tetraphenyl pyrrol and tetraphenyl furfurane, the so-called *lepidene*.

a,β-**Dibenzoyl Styrene,** *Anhydroacetophenone Benzil*, $C_6H_5CO . CH : C(C_6H_5)COC_6H_5$, melting at 129°, is obtained from benzil and acetophenone by the action of caustic potash. When heated it rearranges itself by the migration of a phenyl group into the isomeric *tri-phenylcrotolactone*, melting at 118°:

$$\underset{\text{Dibenzoyl Styrene}}{C_6H_5CO . C(C_6H_5) : CHCOC_6H_5} \longrightarrow \underset{a,a,\gamma\text{-Triphenylcrotolactone.}}{(C_6H_5)_2\overset{CO\text{——}O}{\overset{|}{C}} . CH : \overset{|}{C}C_6H_5}$$

Dibenzoyl Stilbene, *acicular oxylepidene*, $C_6H_5CO . C(C_6H_5) : C(C_6H_5)COC_6H_5$, melting at 220°, resulting from the oxidation of lepidene (see above) with nitric acid, or of thionessal (p. 370) with potassium chlorate and hydrochloric acid, also yields, on heating, *tetraphenylcrotolactone, tabular oxylepidene*, melting at 136°:

$$\underset{\text{Dibenzoyl Stilbene}}{C_6H_5COC(C_6H_5) : C(C_6H_5)COC_6H_5} \longrightarrow \underset{a,a,\beta,\gamma\text{-Tetraphenylcrotolactone.}}{(C_6H_5)_2\overset{CO\text{————}O}{\overset{|}{C}} . C(C_6H_5) : \overset{|}{C}(C_6H_5)}$$

Consult B. **24**, 510; **25**, R. 418, for the action of phenylhydrazine upon dibenzoyl styrene and stilbene. Bidesyl results from the reduction of dibenzoyl-stilbene.

Diphenyltetraketone, $C_6H_5 . CO . CO . CO . CO . C_6H_5 (+ H_2O)$, melting at 87°, is *red* in color when hydrous, and yellow when anhydrous. It is formed in the oxidation of **Benzoyl Formoïn,** $C_6H_5 . CO . CO . CH(OH)COC_6H_5$, melting at 170°, which is produced like benzoïn from benzaldehyde by condensing two molecules of phenyl glyoxal with potassium cyanide. Benzoyl formoïn also results readily from the action of soda upon iso-nitroso-acetophenone acetate, $C_6H_5 . CO . CH : NO . COCH_3$. Substituted diphenyltetraketones have been similarly prepared (B. **25**, 3468).

Diphenyltetraketone is a member of the following homologous series:

Diphenyl Diketone, Benzil,	$C_6H_5CO . COC_6H_5$ (p. 373).
Diphenyl Triketone,	$C_6H_5 . CO . CO . CO . C_6H_5$ (p. 379).
Diphenyl Tetraketone,	$C_6H_5 . CO . CO . CO . CO . C_6H_5$.

Hydroxylamine forms but one 1,4-*dioxime* $[C_6H_5C(NOH)CO]_2$, melting at 176° with decomposition; the 2,3-*dioxime* or *dibenzoylglyoxime*, $C_6H_5 . COC(NOH)C(NOH)CO-C_6H_5$, melting with decomposition at 108°, results from the reduction of its peroxide, which is formed in the interaction of nitric acid and acetophenone. Hydroxylamine converts the 2,3-dioxime into *diphenyltetraketoxime*, $C_6H_5[C(NOH)]_4C_6H_5$, melting at 225° (B. **26**, 528).

Carboxylic Acids: *a*-**Phenylcinnamenyl Acrylic Acid,** $C_6H_5CH : CH . CH : C(C_6H_5)COOH$, melting at 188°, and its dioxymethylene derivative, *a*-**Phenyl Piperic Acid,** melting at 209°, are obtained from cinnamic aldehyde and piperonyl acroleïn with phenylacetic acid by means of Perkin's reaction (B. **28**, 1189).

The ester of **benzoyl phenacyl-acetic acid,** *a,β-dibenzoyl propionic acid*, $C_6H_5 . CO . CH_2 . CH(CO . C_6H_5)COOR$, is obtained from benzoyl acetic ester with phenacyl bromide (p. 249). In the ketone decomposition it yields diphenacyl (p. 380); and by the acid decomposition, benzoyl propionic acid (p. 260) and benzoic acid. **Iso-oxalyl-**

dibenzylketone, melting at 240–242°, may be referred to benzoyloxalylphenylacetic acid, $C_6H_5 . CH_2 . CO . CO . CH(C_6H_5) . COOH$, isomeric with dibenzoylpropionic acid. It is formed on heating oxalyldibenzylketone (p. 378) beyond its melting point (A. **284**, 293):

$$\underbrace{C_6H_5C : C(OH) . CO . CH . C_6H_5}_{CO} \longrightarrow \begin{matrix} C_6H_5C : C(OH) . C : CH . C_6H_5 \\ CO \text{———} O \end{matrix}$$

Alkalies convert isoxalylbenzylketone, just like pulvic acid richer in CO_2, into dibenzyl glycollic acid.

Dibenzylidene Succinic Acid, $C_6H_5CH : C(COOH) . C(COOH) : CHC_6H_5$, melting with decomposition at 201°, and **benzylidene-γ-diphenylitaconic acid,** $(C_6H_5)_2C : C\text{-}(COOH) . C(COOH) : CH . C_6H_5$, are obtained by the condensation of succinic ester (1) with two molecules of benzaldehyde, and (2) with benzophenone and benzaldehyde by means of sodium ethylate (B. **30**, 94).

Dibenzoyl Succinic Acid, $\begin{matrix} C_6H_5 . CO . CH . CO_2H \\ C_6H_5 . CO . CH . CO_2H \end{matrix}$. Its *ethyl ester*, melting at 129°, is obtained from sodium benzoyl acetic ester by the action of iodine, just as we form diaceto-succinic ester from acetoacetic ester. By the elimination of water there results *diphenyl-furfurane dicarboxylic ester*. The esters of the acid appear in three forms, of which the unstable (*labile*) variety, soluble in alkalies, is probably the enol-form, $[C_6H_5\text{-}C(OH) : C(COOH\text{-}]_2$, while the other two represent the syn- and anti-modifications of the keto-form (B. **29**, R. 962).

Diphenyloxalyl Diacetic Acid, *Diphenylketipic Acid*, $COOH . CH(C_6H_5)CO . CO . CH(C_6H_5)COOH$, is isomeric with dibenzoylsuccinic acid. Its *dinitrile*, melting at 270° with decomposition, is produced by the condensation of oxalic ester with two molecules of benzyl cyanide. When saponified with hydrochloric or sulphuric acid it yields not the free acid, but passes at once into its anhydride, a *monolactone*, **Pulvic Acid,** $\overline{OOC . CH(C_6H_5)CO . C} : C(C_6H_5)COOH$, melting at 214°, and a *dilactone*, $\overline{OOC . C(C_6H_5) : C} . \underline{C : C(C_6H_5)COO}$. Pulvic acid may also be prepared from **Vulpic Acid,** $C_{19}H_{14}O_5$, consisting of yellow prisms, melting at 110°, and found in a certain moss and in the lichen *Cetraria vulpina*, by boiling it with lime-water. Sodium ethylate converts pulvic acid back into salts of vulpic acid. The latter is therefore very probably to be regarded as a methyl ether of pulvic acid (B. **27**, R. 869; A. **288**, 14). Zinc-dust and ammonia reduce pulvic acid to **Hydrocornicularic Acid,** *α,δ-Diphenyl-lævulinic Acid*, $C_6H_5 . CH_2 . CO . CH_2 . CH(C_6H_5)COOH$, melting at 134°. Distilled with lime, it yields phenylethylbenzyl ketone (p. 380), and when heated with caustic potash the products are toluene and phenylsuccinic acid (p. 262). Boiling alkalies decompose pulvic and vulpic acids into $2CO_2$ and dibenzylglycollic acid. If it be assumed that diphenylketipic acid is formed at first, then this reaction, discarding the evolution of CO_2, is an analogue of the benzilic acid transposition (p. 374):

$$\begin{matrix} C_6H_5 . CH(COOH) . CO \\ C_6H_5 . CH(COOH) . CO \end{matrix} \xrightarrow[-2CO_2]{+H_2O} \begin{matrix} C_6H_5 . CH_2 \\ C_6H_5 . CH_2 \end{matrix} \!\!> C(OH)COOH.$$

Ethane-dibenzoyl-o₂-dicarboxylic Acid, $COOH . C_6H_4CO . CH_2 . CH_2 . CO . C_6H_4 . COOH$, is another isomeride of dibenzoylsuccinic acid. It melts at 166°. It is made by boiling **ethine diphthalyl,** $\overline{O . OC . C_6H_4 . C} : CH . CH : \overline{C . C_6H_4 . COO}$, melting above 350°, the *dilactone* corresponding to it, with alkalies. Ethine diphthalyl results from the condensation of two molecules of phthalic anhydride with succinic acid when two molecules of carbon dioxide are split off (B. **17**, 2770). Sodium alcoholate rearranges it into bisdiketohydrindene (p. 388).

VII. ω,ω-DIPHENYLPENTANE GROUP.

The hydrocarbons of this group are not known.

Ketones: **Dibenzylidene Acetone**, $C_6H_5CH : CH . CO . CH : CH . C_6H_5$, yellow needles, melting at 112°, is formed when acetone and benzaldehyde are treated with sodium hydroxide. In the first step benzal acetone is produced (p. 272):

$$CH_3.CO.CH_3 \xrightarrow{C_6H_5CHO} C_6H_5CH{:}CH.CO.CH_3 \xrightarrow{C_6H_5CHO} C_6H_5CH{:}CH.CO.CH{:}CH.C_6H_5.$$

Di-o-cumarketone, $(OHC_6H_4CH : CH)_2CO$, melting at 160°, is produced in the form of its diglycose compound by the condensation of helicine (see this) with acetone. **Cinnamylidene Acetophenone**, $C_6H_5CH : CH . CH : CH . COC_6H_5$, from cinnamic aldehyde and acetophenone, melts at 103°; its *oxime*, melting at 131°, is condensed to aa_1-diphenylpyridine upon the application of heat (B. **28**, 1730).

1,5-Diketones of this group are obtained by condensing benzaldehydes (1 mol.) and acetophenones (2 mols.) with sodium hydroxide: **benzylidene diacetophenone**, $C_6H_5CH(CH_2 . CO . C_6H_5)_2$, melting at 85°, and **o-oxybenzylidene diacetophenone**, $(OH)[2]C_6H_4(CH_2 . CO . C_6H_5)_2$, melting at 131°. By varying the conditions and condensing two molecules of benzaldehyde with three molecules of acetophenone, two isomeric **dibenzylidene-triacetophenones**, $(C_6H_5CH)_2(CH_2COC_6H_5)_3$, melting at 198° and 256° respectively, are produced.

Benzamarone, *Benzylidenebisdesoxybenzoïn*, $C_6H_5COCH(C_6H_5)CH(C_6H_5) . CH(C_6H_5)COC_6H_5$ (?), exists in two modifications, melting at 219° and 180°. It is prepared by condensing benzaldehyde with desoxybenzoïn, as well as by the addition of desoxybenzoïn to benzylidenedesoxybenzoïn (p. 379) by the aid of sodium ethylate. Similarly, desoxybenzoïn attaches itself to the unsaturated unions of other oleфine derivatives—*e. g.*, α-phenylcinnamo nitrile, benzalacetoacetic ester, benzalbenzoylpyroracemic ester, etc. (B. **25**, 1087). By decomposition with sodium ethylate benzamarone yields the sodium salt of *amaric acid*, $C_{23}H_{20}O_3$, and with sodium isobutylate it forms *dimethylamaric acid*, $C_{25}H_{26}O_3$ (A. **275**, 50).

The dry distillation of benzamarone produces desoxybenzoïn, benzylidene desoxybenzoïn, and a body isomeric with the latter (B. **26**, 818). Hydroxylamine changes it quite readily into *pentaphenylpyridine*.

Carboxyl derivatives of the ω,ω-diphenylpentane group: **Diphenacyl Acetic Acid**, $(C_6H_5COCH_2)_2CH . CO_2H$, melting at 133°, is obtained from **diphenacyl malonic ester**, $(C_6H_5COCH_2)_2C(CO_2R)_2$, or **diphenacyl acetoacetic ester**, $(C_6H_5COCH_2)_2C(COCH_3)COOC_2H_5$, melting at 83°, the reaction-products from phenacyl bromide upon malonic ester and acetoacetic ester (B. **22**, 3225). Diphenacyl acetic acid, being an ε-diketone, forms a *pyridine*-derivative with ammonia (B. **29**, 798).

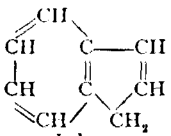
VIII. ω,ω-DIPHENYL HEXANE GROUP AND HIGHER HOMOLOGUES.

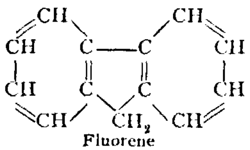
Oxalyldiacetophenone, $C_6H_5COCH_2COCOCH_2COC_6H_5$, melting at 180°, is formed in the condensation of two molecules of acetophenone and oxalic ester with sodium alcoholate. Consult B. **28**, 1206, for the reduction-products of this tetraketone.

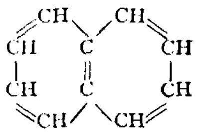
ω,ω-Diphenyl Diketohexane, $(C_6H_5COCH_2CH_2)_2$. **Diphenyl Diketo-octane**, $(C_6H_5COCH_2CH_2CH_2)_2$, and **Diphenyl Diketononane**, $(C_6H_5CO . CH_2 . CH_2 . CH_2)_2CH_2$, are prepared from the chlorides of adipic acid, sebacic acid, and azelaic acid by means of benzene and aluminium chloride (B. **29**, R. 1157). **Cinnamylene benzylidene acetone**, $C_6H_5CH : CH . CH : CH . COCH : CHC_6H_5$, melting at 106°, is derived from ω,ω-diphenylheptane. It is formed from cinnamylene acetone and benzaldehyde (B. **29**, 615).

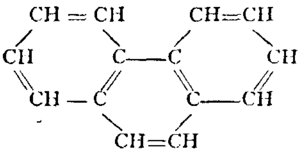
B. CONDENSED NUCLEI.

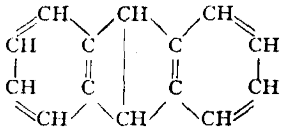
The condensed nuclei to be discussed in the following section are characterized by the fact that in them C-atoms of benzene nuclei participate in the formation of other carbocyclic rings—*e. g.*:


Indene


Fluorene


Naphthalene

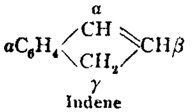

Phenanthrene

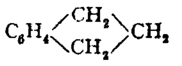

Anthracene.

Although these condensed nuclei, as a rule, continue to manifest their aromatic character, they do, in harmony with their peculiar structure, exhibit in their behavior a series of wide differences from the true benzene compounds (see naphthalene). They are eventually, by suitable oxidations, changed like the homologues of benzene into benzene carboxylic acids. The parent hydrocarbons of these groups occur, like benzene, chiefly in coal-tar, from which they are obtained in greater or lesser amount. Naphthalene is technically important; this is especially true of anthracene, the hydrocarbon of alizarin.

The carbocyclic derivatives of the tri-, tetra-, and pentamethylene series constitute the transition from the fatty bodies with open chain to the benzene derivatives. Similarly, the indene and the hydrindene compounds form the transition members from the fatty-aromatic substances with open side-chains to those which contain several condensed benzene nuclei. They represent the coalescence of a benzene nucleus with the five-membered pentene. Very probably pseudophenyl acetic acid (p. 196) contains a united benzene and trimethylene ring.

1. INDENE AND HYDRINDENE GROUP.


Indene


Hydrindene.

Indene has received its name from indol, because of its similarity to the latter in structure. By introducing NH for the methylene group of indene the formula of indol results.

Indene, C_9H_8, is an oil, boiling at 178°; its specific gravity equals 1.040 at 15°. It occurs, together with coumarone, to which it is very similar in its behavior (B. **28**, 114), in that fraction of coal-tar boiling at 176–182°, and can be extracted from it by means of its

picric acid derivative (B. **23**, 3276). Very appreciable amounts of indene are also present in the condensation products resulting from the chilling of illuminating gas (B. **28**, 1331). It can also be obtained by the distillation of the calcium salt of synthetic hydrindene carboxylic acid (p. 387) (B. **27**, R. 465). Sulphuric acid resinifies indene. Chlorine and bromine unite with it to dibrom- and dichlorhydrindenes. Like the terpenes (p. 309), it also combines with NOCl and N_2O_3, forming **indene nitrosites**, the α-variety melting with decomposition at 108°, and the β-form at 137° (B. **28**, 1331). Metallic sodium and alcohol reduce indene to hydrindene. When heated to redness two molecules of indene unite, with the exit of four hydrogen atoms, to chrysene (see this). Bz.-**Brom-indene**, $C_6H_3Br(C_3H_4)$, boiling at 243°, is formed from hydrindene and bromine (B. **26**, 2251). It yields bromphthalic acid upon oxidation.

Indene derivatives are obtained synthetically by the following methods, which to some extent recall the syntheses of the pentamethylene compounds :

(1) Benzene compounds, having the group $C_6H_5 . C . C . CO$, split off water and condense to indene derivatives : (a) Nitro-α-alkyl cinnamic aldehydes yield amido-β-alkyl indenes (B. **22**, 1830):

$$NO_2 . C_6H_4 \begin{matrix} \diagup OCH \diagdown \\ \diagdown CH \diagup \end{matrix} C . CH_3 \longrightarrow NH_2 . C_6H_3 \begin{matrix} \diagup CH \diagdown \\ \diagdown CH_2 \diagup \end{matrix} C . CH_3$$

Nitro-α-methylcinnamic Aldehyde Amido-β-methylindene.

Similarly, benzyl acetone and benzyl acetoacetic ester yield γ-methylindene and γ-methylindene-β-carboxylic acid (B. **20**, 1574; A. **247**, 157) when they are heated with sulphuric acid :

$$C_6H_5 \begin{matrix} OC - CH_3 \\ \diagdown CH_2 > CH_2 \end{matrix} \longrightarrow C_6H_4 \begin{matrix} \diagup C = CH_3 \\ \diagdown CH_2 \diagup CH \end{matrix};$$

Benzyl Acetone *γ-Methyl Indene*

$$C_6H_5 \begin{matrix} OC - CH_3 \\ \diagdown CH_2 > CH . CO_2H \end{matrix} \longrightarrow C_6H_4 \begin{matrix} \diagup C = CH_3 \\ \diagdown CH_2 \diagup C . CO_2H \end{matrix}$$

Benzylacetoacetic Acid Methylindene Carboxylic Acid.

(b) Substituted cinnamic acids yield *indone* derivatives when they are treated with hot sulphuric acid, just as the hydrocinnamic acids, alkylized in the nucleus and in the side-chain, yield *dihydroindones*. Cinnamic and hydrocinnamic acids themselves react with as little readiness as cinnamic aldehyde (A. **247**, 140; B. **25**, 2095, 2129):

$$C_6H_5 \begin{matrix} HOCO \diagdown \\ \diagdown CBr = \diagup \end{matrix} CBr \longrightarrow C_6H_4 \begin{matrix} \diagup CO \diagdown \\ \diagdown CBr \diagup \end{matrix} CBr ;$$

Dibromcinnamic Acid Dibromindone

$$C_6H_5 \begin{matrix} HOCO \diagdown \\ \diagdown CH_2 - \diagup \end{matrix} CH . C_6H_5 \longrightarrow C_6H_4 \begin{matrix} \diagup CO \diagdown \\ \diagdown CH_2 \diagup \end{matrix} CH . C_6H_5$$

α-Phenylhydrocinnamic Acid β-Phenylhydrindone.

(2) The *hydrindene* derivatives have been obtained in the same manner as the tetra- and pentamethylene derivatives (p. 21) : by the action of xylylene halides upon malonic ester and sodium alcoholate (B. **17**, 125 ; **18**, 378) :

$$C_6H_4 < \begin{matrix} CH_2Br \\ CH_2Br \end{matrix} + CNa_2 < \begin{matrix} CO_2R \\ CO_2R \end{matrix} = C_6H_4 < \begin{matrix} CH_2 \\ CH_2 \end{matrix} > C < \begin{matrix} CO_2R \\ CO_2R \end{matrix}$$

(3 a) The formation of $\alpha\gamma$-diketohydrindenes from o-phthalic esters and fatty acid esters or ketones (A. **252**, 72 ; B. **27**, 104, R. 19) corresponds to the condensation of oxalic esters to pentamethylene derivatives :

$$C_6H_4 < \begin{matrix} COOR \\ COOR \end{matrix} + H_3C . CO_2R \longrightarrow C_6H_4 < \begin{matrix} CO \\ CO \end{matrix} > CH . CO_2R.$$

(3 b) The phthalide compounds (pp. 240, 290) of the formula $C_6H_4\left\langle\begin{matrix}C{=\!=}CHR\\ CO{>}O\end{matrix}\right.$, formed from phthalic anhydride and fatty acids, are transposed by sodium alcoholates into the sodium derivatives of the isomeric diketohydrindenes (B. **26**, 954, 2576):

$$C_6H_4\left\langle\begin{matrix}C{=\!=}CHBr\\ CO{>}O\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}CO\\ CO\end{matrix}\right\rangle CHR.$$

(4) The formation of dihydroindones by the distillation of salts of o-phenylene diacetic acid and o-hydrocinnamic acid (B. **26**, 222, R. 708) corresponds to the cyclic ketone formation of dicarboxylic acids of the adipic acid series (p. 21):

$$C_6H_4{<}\begin{matrix}CH_2.COOH\\ CH_2.COOH\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH_2\\ CH_2\end{matrix}{>}CO;$$

$$C_6H_4{<}\begin{matrix}CH_2-CH_2.COOH\\ COOH\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH_2\\ CO\end{matrix}{>}CH_2.$$

(5) The formation of indene derivatives from naphthalene derivatives is rather remarkable; a six-membered benzene-ring is rearranged to a ring of five members—similar to the production of pentamethylene derivatives from the benzenes, or fluorene compounds from phenanthraquinone. This change occurs by the action of chlorine or hypochlorous acid upon the naphthols, naphthoquinones, amidonaphthols, etc. The first product consists of naphthalene keto-derivatives with the groups —CO.CO— or CO.CCl_2—; these sustain the decomposition (B. **20**, 2890; **21**, 2719). Thus, dichlor-β-naphthoquinone yields dichloroxyindene carboxylic acid:

$$C_6H_4\left\langle\begin{matrix}CO-CO\\ CCl=CCl\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}C(OH)\left\langle\begin{matrix}CO_2H\\ CCl\end{matrix}\right.\\ CCl{=\!=}\end{matrix}\right.$$

Dichlor-β-naphthoquinone — Dichloroxyindene-carboxylic Acid.

Indene Derivatives: γ-**Methyl Indene,** $C_6H_4:C_3H_3.CH_3$, boiling at 206°, is obtained synthetically from benzyl acetone, and by the elimination of CO_2 from its carboxylic acid. *Bz.-Amido-β-methyl-, ethyl-, isopropyl indenes* melt at 98°, 89°, and 84° (see above) respectively.

β-**Indene Carboxylic Acid,** $C_6H_4:C_3H_3.CO_2H$, melting at 222–230°, is produced by the action of bromine at 100° upon a chloroform solution of hydrindene carboxylic acid (see below).

γ-**Methyl-β-indene Carboxylic Acid,** melting at 200°, is obtained from benzylacetoacetic ester.

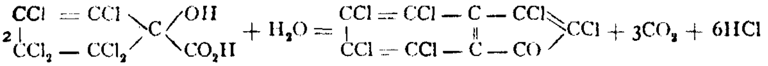
β,γ-**Dichlor-α-oxyindene Carboxylic Acid,** melting at 100°, is obtained from β-dichlornaphthoquinone. Chromic acid oxidizes it to dichlorindone. It is changed to chlorindone carboxylic acid when digested with concentrated sulphuric acid (B. **28**, R. 279).

α,β-**Diphenylindone,** $C_6H_4\left\langle\begin{matrix}C(C_6H_5)\\ CO\end{matrix}\right\rangle C(C_6H_5)$, garnet-red crystals, melting at 151°, is produced, together with triphenylacrylic acid (p. 378), when benzophenone chloride is condensed with phenylacetic ester. It yields triphenyl propane upon reduction. It is decomposed into α,β-diphenylvinyl-o-benzoic acid when fused with caustic potash. It can be recovered from this as well as from triphenylacrylic acid on heating with zinc chloride (B. **30**, 1281).

β,γ-**Dichlor- and Dibromindone,** $C_6H_4:C_3Br_2O$, melting at 90° and 123°, have been obtained synthetically from dichlor- and dibromcinnamic acids. The γ-chlorine atom in these compounds is readily replaced by OH or NHR on digesting them with caustic soda, or fatty or aromatic amines. β-**Chlor- and β-Brom-γ-oxyindone melt at 114° and 119°.** β-**Chlor- and Bromanilido-indone melt at 204° and 170°.**

Perchlorindone, $C_6Cl_4:C_3Cl_2O$, **melting at 149°, is produced by a peculiar reaction**

from a *pentene*-derivative, hexachloroxy-R-pentene carboxylic acid, the decomposition product of hexachlordiketo-R-hexene, on digesting it with water or with a solution of sodium acetate (A. **272**, 243; B. **28**, 521):



Hexachloroxypentene Carboxylic Acid — Perchlorindone.

Hydrindene Derivatives: **Hydrindene**, $C_6H_4 : C_3H_6$, is an oil, boiling at 177°. It results when indene is reduced with sodium and alcohol.

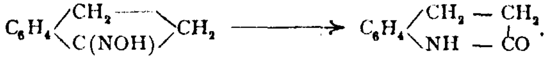
Dichlorhydrindene is an oil. **Dibromhydrindene**, $C_6H_4 : C_3H_4Br_2$, melts at 44°. They yield **chlor- and bromoxyhydrindenes**, melting at 129° and 131°, when digested with water. Ammonia converts the latter bodies, in the cold, into **amido-oxyhydrindene**, melting at 133°, which nitrous acid transposes into β,γ-**dioxyhydrindene**, *hydrindene glycol*, $C_6H_4 : C_3H_4(OH)_2$, melting at 120° (B. **26**, 1539).

Hydrindene-β-methyl-, ethyl-, and phenylketones are formed in the distillation of hydrindene carboxylic acid with benzoic acid, propionic acid, and acetic acid (B. **26**, 2251).

Hydrindene-β carboxylic Acid, $C_6H_4(CH_2)_2CH . CO_2H$, melting at 130°, is converted by distillation of its salts into indene, by bromine into indene-carboxylic acid, and is oxidized by $KMnO_4$ to o-carbophenylglyoxylic acid (p. 265). It results when CO_2 is eliminated from **hydrindene-β-dicarboxylic acid**, melting at 199°. The ester of the latter acid may be obtained synthetically from xylylene bromide and malonic ester.

β-Acethydrindene Carboxylic Ester, $C_6H_4(CH_2)_2C{<}{}^{COCH_3}_{CO_2R}$, is obtained from xylylene bromide and acetoacetic ester.

α-Hydrindone, $C_6H_4{<}{}^{CH_2}_{CO}{>}CH_2$, melting at 41° and boiling at 244°, is obtained in the dry distillation of o-carbohydrocinnamic acid (p. 245) as well as from o-cyanhydrocinnamic ester (p. 245) upon digesting with concentrated hydrochloric acid. The *phenylhydrazone* melts at 131°. The *oxime*, melting at 146°, is changed by reduction to *α-amidohydrindene*, melting at 220°, which N_2O_3 converts into *α-oxyhydrindene*, melting at 54° (B. **26**, R. 708). Phosphorus pentachloride converts α-hydrindonoxime into hydrocarbostyril (Beckmann's transposition) (B. **27**, R. 598):



Hydrindone Azine, $C_9H_8 : N . N : C_9H_8$, melting at 165°, results from the action of hydrazine upon the oxime. Nitrous acid converts hydrindone into **isonitrosohydrindone**, $C_6H_4{<}{}^{CH_2}_{CO}{>}C = NOH$, melting with decomposition at 210°. This phenylhydrazine changes to an *osazone*, melting at 229°. The latter is isomeric with the dihydrazone obtained from *α,γ-diketohydrindene*. It yields **β-amido-α-hydrindone** when it is reduced (B. **29**, 2605, R. 869; C., 1897, I, 860).

When o-, m-, and p-methylhydrocinnamic acids are heated they yield o-, m-, and p-**Methyl-α-hydrindones**. The constitution of the latter is deduced from their oxidation to the various methyl-o-phthalic acids. Bz.-**Chlor-**, **brom-**, **iod-**, and **nitrohydrindones** behave similarly (B. **25**, 2095).

β-Methyl-α-hydrindone, melting at 168° (11 mm.), and **β-Phenyl-α-hydrindone**, melting at 78°, are obtained from α-methyl and phenylhydrocinnamic acids. When its ethereal solution is shaken with caustic soda β-phenylhydrindone is changed partly to **β-phenyloxyhydrindone**, melting at 129°, and in part by rupture of the ring into desoxybenzoïn-o-carboxylic acid, $C_6H_4(CO . OH) . CH_2 . COC_6H_5$ (p. 376) (B. **26**, 2095). **γ-Phenyl-α-hydrindone**, melting at 78°, is prepared from **β,β-diphenyl-propionic acid** (B. **26**, 2128).

Tetrachlor-α-hydrindone, $C_6H_4 : C_3Cl_4O$, melting at 108°, is the addition product of

chlorine and dichlorindone (p. 387). It is readily decomposed by digestion with alcoholic sodium hydrate into o-trichlorvinylbenzoic acid (p. 273). **Chlordibrom-hydrindone-γ-carboxylic Acid**, $C_6H_4 : [C_3ClBr_2O(COOH)]$, melting at 171°, is made from chlorindone-γ-carboxylic acid (p. 387) and bromine. It is similarly decomposed into bromchlormethylene-homophthalic acid (p. 393).

β-Hydrindone, $C_6H_4(CH_2)_2CO$, melting at 61° and boiling with decomposition at 220–225°, is obtained from calcium o-phenylene diacetate (p. 245). Its *hydrazone* melts at 120°. Its *oxime*, melting at 155°, yields *β-amidohydrindene* upon reduction (B. 26, R. 709).

α,γ-Diketohydrindene, $C_6H_4(CO)_2CH_2$, melting with decomposition at 130°, is obtained from its carboxylic acid (below). It consists of colorless needles, which dissolve readily with a yellow color in alkalies. The hydrogen atoms of the methylene groups placed between the two keto-groups have an acid nature. Phenylhydrazine converts it into a *monohydrazone*, melting at 163°, and a *dihydrazone*, $C_6H_4(C : NNH\text{-}C_6H_5)_2CH_2$, melting at 171°. Diazobenzene chloride converts the monohydrazone into a *triketohydrindene*, $C_6H_4(CO)_2C : NNHC_6H_5$, which is also prepared by the decomposition of *benzaldiketohydrindene*, $C_6H_4(CO)_2C = CHC_6H_5$, a condensation product of benzaldehyde and diketohydrindene, with phenylhydrazine.

3,4-Dioxybenzaldiketohydrindene, melting at 257°, and prepared by the condensation of protocatechuic aldehyde and diketohydrindene, is a dye (B. 30, 1185). When diketohydrindene is digested alone, or when it is boiled with water, **anhydrobisketohydrindene**, $C_6H_4(CO)_2C = C<{C_6H_4 \atop CH_2}>CO$, is formed. This yields intensely colored metallic derivatives. Phenylhydrazine resolves this substance into two molecules of diketohydrindene-dihydrazone (A. 277, 362).

β-Methyldiketohydrindene, $C_6H_4(CO)_2CH . CH_3$, melting at 85°, is prepared from its carboxylic acid, as well as by the rearrangement of ethidene phthalide (p. 286). Methyl iodide converts its sodium derivative into **β-dimethyldiketohydrindene**, $C_6H_4\text{-}(CO)_2C(CH_3)_2$, which can also be obtained by the action of methyl iodide upon the di-sodium compound of the diketohydrindene carboxylic acid. **β-Phenyldiketohydrindene**, melting at 145°, is made from benzalphthalide, and **Bisdiketohydrindene**, $C_6H_4\text{-}(CO)_2CH . CH . (CO)_2C_6H_4$, from ethine diphthalyl (p. 382). The latter consists of violet-colored needles, melting above 350° (B. 26, 2576; 29, 2376). Potassium persulphate oxidizes potassium diketohydrindene to **diphthalyl ethene**, $C_6H_4(CO)_2C : C\text{-}(CO)_2C_6H_4$, which has been designated *indenigo* because its structure resembles that of indigo. It forms alizarin-red needles, which sublime with decomposition at 200° (B. 30, 386).

β-Acetyl- and Benzoyldiketohydrindene, $C_6H_4(CO)_2CH . COR$, **melting at 110° and 108°, are formed from phthalic esters with acetone and acetophenone.** They appear to be very easily decomposed by alkalies (B. 27, 104).

β-Dichlordiketohydrindene, $C_6H_4(CO)_2CCl_2$, melting at 125°, is produced by the action of chlorine upon γ-oxychlorindone (p. 387). Dilute caustic soda decomposes it quite readily into o-phthalic acid (B. 21, 491, 2380).

Diketohydrindene Carboxylic Ester, $C_6H_4(CO)_2CH . CO_2R$, melting at 75–78°, formed from phthalic ester by means of acetic ester and sodium alcoholates, is converted very readily, just like the preceding acid, into diketohydrindene (B. 26, 954).

β-Methyldiketohydrindene-carboxylic Ester, $C_6H_4(CO)_2C(CH_3)CO_2R$, **is formed from phthalic ester and propionic ester.**

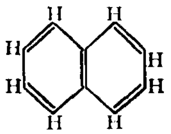
Fluorene is a *dibenzopentene* resulting from the union of the pentene nucleus with two benzene nuclei. It will be considered in conjunction with *chrysene-fluorene* and *picene-fluorene* after the condensed nuclei of the phenanthrene group (pp. 413, 416)—phenanthrene, chrysene, and picene **—to which the two first-named bodies are intimately related.**

2. NAPHTHALENE GROUP.*

Garden (1816) discovered naphthalene, $C_{10}H_8$, among the distillation products of coal-tar. It shows great similarity to benzene, from which it differs in constitution by C_4H_2. Like benzene, it is produced by the action of intense heat upon various carbon compounds; hence its occurrence in coal-tar. Numerous derivatives are obtained from it by the replacement of its hydrogen atoms; they are very similar to the benzene compounds. Only the most important of them will be considered in the following sections.

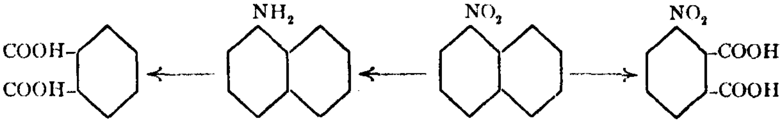
CONSTITUTION OF THE NAPHTHALENE NUCLEUS.

The deportment of naphthalene is satisfactorily explained by the formula first suggested by Erlenmeyer, Sr. (A. **137**, 346):



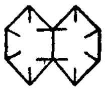
It consists of two benzene nuclei, having in common two carbon atoms occupying the ortho position. Graebe (1866) proved the correctness of the formula (A. **149**, 20).

The oxidation of naphthalene to o-phthalic acid shows the presence of a benzene nucleus (pp. 36, 239). Further, the oxidation of dichlornaphthoquinone, $C_6H_4 : C_4Cl_2O_2$, also yields o-phthalic acid. If, however, dichlornaphthoquinone is converted by PCl_5 into tetrachlornaphthalene, this, upon oxidation, will become tetrachlor-o-phthalic acid. In the second instance, therefore, the benzene nucleus, which in the first case was unattacked, is now oxidized. A perfectly similar method of demonstration, to which reference has already been made (p. 36), is as follows: Nitronaphthalene, obtained by nitration of naphthalene, yields nitro-o-phthalic acid; whereas amidonaphthalene, resulting from the reduction of the preceding nitronaphthalene, yields o-phthalic acid:



Hence it follows that naphthalene must consist of two symmetrically condensed benzene nuclei. For other formulas, like the *central formula* of Bamberger, the formula of Armstrong, etc., consult B. **23**, R. 337, 692; **24**, R. 651, 728:

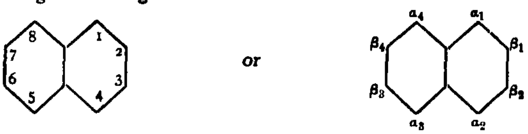
Bamberger.

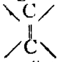


Armstrong.

* "Tabellarische Uebersicht der Naphtalinderivate" von Reverdin und Fulda, Basel, Genf, Lyon, 1894.

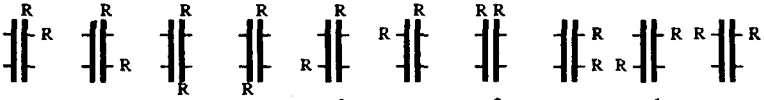
Isomerisms of the Naphthalene Derivatives.—The isomerisms of the derivatives of naphthalene conditioned by this formula agree with the facts. The substituents are designated according to the diagram:



The replacement of an H-atom in naphthalene can give rise to two isomeric mono-derivatives, distinguished as α- and β-derivatives according as the substituent is adjacent to the complex  common to both groups, or separated from it by a CH-group. The positions 1, 4, 5, 8 (α_1, α_2, α_3, α_4) on the one side, and 2, 3, 6, 7 (β_1, β_2, β_3, β_4) are equivalent. Liebermann (A. 183, 254) and Atterberg (B. 9, 1736) have adduced proof of the equivalence of the four α-positions. The method adopted is similar to that followed in demonstrating the equal value of the benzene hydrogen atoms (p. 32).

Whether a substituent occupies the α- or β position is mainly determined by its oxidation to a corresponding o-phthalic acid derivative. Thus, if [1,2,3]-nitrophthalic acid is obtained from α-nitrophthalene, the nitro-group must consequently be adjacent to the contact position of the second benzene nucleus in naphthalene. The constitution of α-oxynaphthalene or α-naphthol is evident also from its synthesis by means of phenyl-isocrotonic acid, $C_6H_5 . CH : CH . CH_2 . COOH$ (p. 278). Besides, only α-derivatives of naphthalene can be converted into quinones analogous to p-benzoquinone, as these alone possess a free H-atom in the para-position with reference to the substituent. This latter circumstance also determines still other peculiarities in the behavior of the compounds of naphthalene—*e. g.*, the power of the naphthols and naphthylamines to unite with diazo-bodies, etc. (p. 401).

The disubstitution products of naphthalene, when the substituents are similar, can exist in ten isomeric forms, which are designated by numbers or prepositions (B. 26, R. 533):*



1,2	1,3	1,4	1,5	1,6	1,7	1,8	2,3	2,6	2,7
Ortho-	Meta-	Para-	Ana-	Epi-	Kata-	Peri-		Amphi-	Pros-

The position of the substituents in the diderivatives can very often be determined by the oxidation method, if thereby it can first be ascertained whether the substituents are in the same nucleus (*isonuclear*) or in different nuclei (*heteronuclear*). Isonuclear substitution products with adjacent substituents show in general the same deportment as the ortho-substitution products of benzene, inasmuch as they form similar condensation products (pp. 96, 153, 157, 159). However, a difference appears to exist between positions like 1,2 and 2,3. Thus, only those amidonaphthalenes manifest the ability to form naphthoquinoline rings in which the pyridene-ring can attach itself to α,β- C-atoms. It must be assumed that the double linkages in naphthalene are not so easily displaced as in benzene (p. 39). The behavior of the 1,8- or peri-derivatives is remarkable. Like the o-diderivatives, they exhibit a series of hetero-ring formations.

NAPHTHALENE-RING FORMATIONS.

Naphthalene is produced by pyrogenic condensation from a series of carbon compounds, like *ethylene, acetylene, ether,* etc. Methods of

* In the following diagram the double hexagon of naphthalene is replaced by two parallel lines, as was similarly done with benzene (p. 36).

producing the naphthalene nucleus by processes in which *one* benzene nucleus pre-exists are more important:

(1) A mixture of *benzene* and *acetylene* conducted through a tube heated to redness yields naphthalene (Bull. 7, 306).

(2) It is derived from phenylbutylene, $C_6H_5 . CH_2 . CH_2 . CH : CH_2$, and its dibromide, on leading their vapors over heated lime:

$$C_6H_5 \left\langle \begin{array}{l} CH_2 - CH_2 \\ CH_2 = \overset{|}{C}H \end{array} \right. = C_6H_4 \left\langle \begin{array}{l} CH = CH \\ CH = \overset{|}{C}H \end{array} \right. + 4H.$$

(3) A direct synthesis of the second benzene ring also ensues in a manner analogous to the formation of the trimethylene and tetramethylene ring, and of the hydrindene ring when o-xylylene bromide acts upon disodium-acetylene tetracarboxylic ester (Baeyer and Perkin, B. 17, 448).

First, we get the ester of tetrahydro-naphthalene tetracarboxylic acid, and this by saponification yields tetrahydro-naphthalene dicarboxylic acid. Naphthalene results from the distillation of its silver salt:

$$C_6H_4 \left\langle \begin{array}{l} CH_2Br \\ CH_2Br \end{array} \right. + \begin{array}{l} NaC(CO_2R)_2 \\ Na\overset{|}{C}(CO_2R)_2 \end{array} = C_6H_4 \left\langle \begin{array}{l} CH_2 - C(CO_2R)_2 \\ CH_2 - \overset{|}{C}(CO_2R)_2 \end{array} \right. .$$

(4) What is further noteworthy is the formation of α-naphthol from phenyl-isocrotonic acid when heated (Fittig and Erdmann, B. 16, 43; A. 247, 372; 255, 263; 275, 284; compare formation of indene derivatives, p. 384).

$$\underset{\text{Phenylisocrotonic Acid}}{C_6H_5 \left\langle \begin{array}{l} CH = CH \\ OC(OH) - \overset{|}{C}H_2 \end{array} \right.} = \underset{\alpha\text{-Naphthol.}}{C_6H_4 \left\langle \begin{array}{l} CH = CH \\ C(OH) = \overset{|}{C}H \end{array} \right.} + H_2O.$$

In a perfectly similar manner 5-, 6-, and 7-*chlor*-1-*naphthols* are obtained from o-, m-, and p-*chlorphenylparaconic acids*; 2- and 4-*methylnaphthols* from α- and β-*methylparaconic acids*; α-naphthol-3-methyl ketone (B. 26, 345) from β-*benzal-lævulinic acid*, $C_6H_5 \left\langle \begin{array}{l} CH = CH . CO . CH_3 \\ OC(OH) - \overset{|}{C}H_2 \end{array} \right.$, and 2-phenyl-1,3-dioxynaphthalene is produced when α,γ-diphenylacetoacetic ester, $C_6H_5 \left\langle \begin{array}{l} CH_2 - CO \\ ROCO - \overset{|}{C}H(C_6H_5) \end{array} \right.$, is digested with concentrated sulphuric acid (A. 296, 14).

(5) An interesting formation of α-naphthylamine consists in heating *aniline* with *pyromucic acid* and zinc chloride to 300° (B. 20, R. 221):

$$\underset{\text{Aniline}}{NH_2 . C_6H_5} + \underset{\text{Pyromucic Acid}}{O \left\langle \begin{array}{l} CO_2H . C = CH \\ CH = \overset{|}{C}H \end{array} \right.} = \underset{\alpha\text{-Naphthylamine.}}{NH_2C_6H_3 \left\langle \begin{array}{l} CH = CH \\ CH = \overset{|}{C}H \end{array} \right.} + CO_2 + H_2O.$$

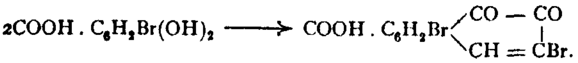
α-Naphthylamine is similarly formed on heating aniline hydrochloride with mannitol under pressure.

(6) Two molecules of styrolene alcohol or phenyl glycol (p. 248) can be condensed by dilute H_2SO_4 to β-phenylnaphthalene (A. 240, 137):

$$C_6H_5 \left\langle \begin{array}{l} CH(OH) . CH_2(OH) \\ \quad\quad\quad + \\ CH_2(OH) - CH(OH)C_6H_5 \end{array} \right. = C_6H_4 \left\langle \begin{array}{l} CH = CH \\ CH = \overset{|}{C} . C_6H_5 \end{array} \right. + 4H_2O.$$

Phenylacetaldehyde is an intermediate product.

(7) The formation of a naphthalene derivative in the oxidation of bromprotocatechuic acid with nitric acid is peculiar. There is produced thereby a dibrom-β-naphthoquinone carboxylic acid (A. **293**, 120):

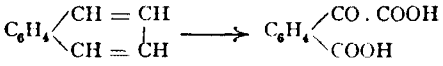


Compare the production of perchlorindone from hexachloroxypentene-carboxylic acid (p. 386).

DECOMPOSITIONS OF THE NAPHTHALENE RING.

Naphthalene and most of its derivatives are converted by energetic oxidants into o-phthalic acid and substituted o-phthalic acids with destruction of one benzene nucleus. The oxidation is made easier by the introduction of an amido-group into the nucleus which is to be oxidized (see p. 389). In many instances it has been possible by moderating the oxidizing action to arrest the intermediate products of this reaction, or even the primary products in the breaking-down of the ring.

1. ***Decomposition by mild oxidation:*** (*a*) Potassium permanganate oxidizes naphthalene to phthalic acid and *phenylglyoxyl-o-carboxylic acid* (p. 265) (B. **28**, R. 490):



Naphthalene — Phenylglyoxyl-o-carboxylic Acid.

(b) α- and β-Naphthols, oxidized with an alkaline permanganate solution, also yield o-carbophenylglyoxylic acid. β-Naphthol with most careful oxidation becomes o-*cinnam-carboxylic acid*, along with other products (M. 10, 115):

β-Naphthol — o-Cinnam-carboxylic Acid.

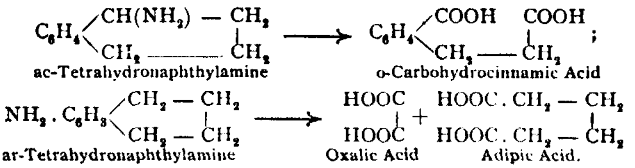
In the oxidation of α-nitronaphthalene with potassium permanganate products appear which, in the process of reduction, yield, among other things, *isatin-carboxylic acid*, $NH_2[3]C_6H_3\left\{\begin{array}{l}[1]COOH\\ [2]COCOOH\end{array}\right.$ (B. 28, 1641). Naphthalic acid (p. 409) becomes *phenylglyoxyldicarboxylic acid* (p. 265).

(c) The decomposition of hydrogenized naphthalene derivatives occurs with special readiness (p. 411); thus, permanganate changes dihydro-β-naphthol into *dihydroisocoumarin-carboxylic acid*, while potassium bichromate oxidizes tetrahydronaphthylene-glycol, in the cold, to *phenylene-o-diacetic acid* (p. 245) (B. **26**, 1833):

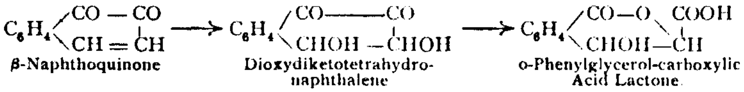
Dihydro-β-naphthol — Dihydroisocoumarin Carboxylic Acid

Tetrahydronaphthylene-glycol — o-Phenylenediacetic Acid.

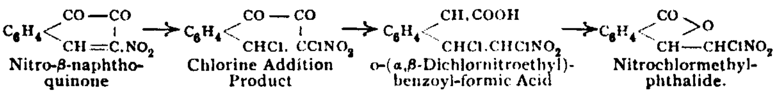
Potassium permanganate oxidizes ac-tetrahydronaphthylamine to o-*hydrocinnam-carboxylic acid* (p. 245); ar-tetrahydronaphthylamine, however, because of the oxidation of its amided benzene nucleus, is changed to *adipic acid* together with oxalic acid (B. 22, 767):



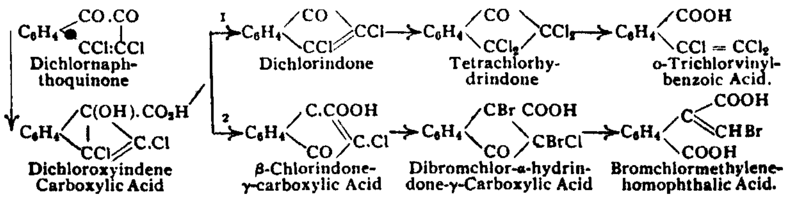
2. *Decomposition by Simultaneous Chlorination and Oxidation.*—The ring-decompositions, produced by the action of chlorine or hypochlorous acid upon β-naphthoquinone and its derivatives, are very numerous. They proceed in lines analogous to the benzene-ring decompositions. Two groups may be distinguished in these changes: either the naphthalene ring first resolves itself into an indene-ring, which subsequently by decomposition is converted into o-diderivatives of benzene, as in the case of dichlornaphthoquinone (see below), or the break-down proceeds without the intermediate formation of indene, as in the case of β-naphthoquinone or nitro-β-naphthoquinone (see below) (Zincke, B. **27**, 2753, etc.). *Examples:* (a) β-Naphthoquinone, by the action of hypochlorous acid, becomes dioxydiketotetrahydronaphthalene, which by the decomposition of the ring changes to the lactone of o-phenylglycerol-carboxylic acid (p. 264) (B. **25**, 3599):



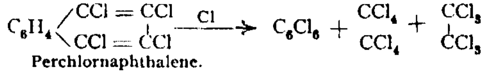
(b) With chlorine nitro-β-naphthoquinone first forms a chlorine addition product, which by ring-decomposition readily passes into o-(α,β-dichlornitroethyl)-benzoyl formic acid. Chromic acid oxidizes the latter, with loss of hydrochloric acid and carbon dioxide, to nitrochlormethylphthalide, which can be directly formed by treating nitroquinone with chlorine and water (B. **25**, R. 732):



(c) Alkalies rearrange 3,4-dichlor-β-naphthoquinone to dichloroxyindene carboxylic acid (p. 386). The latter can be decomposed (1) by changing it to dichlorindone with CrO_3, and tetrachlorhydrindone, the chlorine addition product, when acted upon with alcoholic soda, becomes o-trichlorvinylbenzoic acid; or (2) if the acid be heated to 100–110° with oil of vitriol it is converted into β-chlorindone-γ-carboxylic acid. The bromine addition product of the latter acid is decomposed by alkalies with the formation of α-chlorbrom-methylene-homophthalic acid (B. **28**, R. 279):

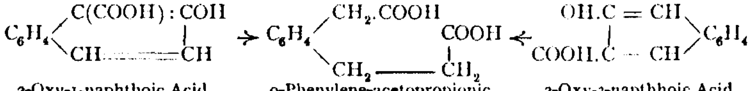


(3) When perchlornaphthalene is heated with $SbCl_5$ to 280–300° it is resolved into perchlorbenzene, tetrachlormethane and hexachlorethane (B. **9**, 1486):



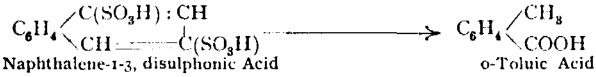
Perchlornaphthalene.

(4) *Decomposition by Reduction in Alkaline Solution.*—A ring-decomposition analogous to that of salicylic acid (p. 47) is that undergone by 2,1- and 2,3-oxynaphthoic acids (p. 408) when their alcoholic solutions are acted upon by metallic sodium (A. **286**, 268):



2-Oxy-1-naphthoic Acid — o-Phenylene-acetopropionic Acid — 2-Oxy-3-napthhoic Acid.

(5) Naphthalene disulphonic acids, naphthylamine- and naphthol-sulphonic acids, containing the substituents in the 1,3-position, sustain a remarkable decomposition into o-toluic acid when they are fused with caustic potash (B. **28**, R. 364):



Naphthalene-1-3, disulphonic Acid — o-Toluic Acid.

m-Cresol (Ch. Z. 1895, Nr. 48) is similarly produced on fusing 1,3,6- and 1,3,8-naphthalene-trisulphonic acids with caustic potash.

Naphthalene, $C_{10}H_8$, melting at 79° and boiling at 218°, occurs in coal-tar, and is obtained by crystallization from that portion boiling from 180–300°. It is purified by distillation with steam and sublimation. It dissolves with difficulty in cold alcohol, readily in hot alcohol and in ether. It crystallizes and sublimes in shining plates. It is characterized by its great volatility and possesses a peculiar odor. It forms a crystalline compound, $C_{10}H_8 . C_6H_2(NO_2)_3 . OH$, with *picric acid*, which melts at 149° (Fritzsche, J. **1857**, 456). m- and p-Dinitrobenzene, trinitrobenzene, trinitrotoluene, etc., form similar double compounds.

Naphthalene is applied technically in the preparation of phthalic acid and dye-substances. It is also used in carburetting water-gas. It is employed for itch, moths, etc., because of its strong antiseptic properties and its stupefying effect upon the lower animals.

As naphthalene has unsaturated linkages it will, under favorable conditions, take up hydrogen and chlorine: the compounds thus produced will be discussed in conjunction with other hydronaphthalene derivatives at the conclusion of the naphthalene group. Naphthalene, like benzene, is chlorinated, nitrated, and sulphonated by halogen, nitric acid, and sulphuric acid. See p. 392 for the naphthalene oxidation products.

Naphthalene Homologues.—The methylated naphthalenes are present in coal-tar. Alkylic naphthalenes also result from the brom-naphthalenes by the action of alkylogens and sodium, and from naphthalene by means of alkyl iodides or bromides and Al_2Cl_6:

		M. P.	B. P.
α-Methyl-naphthalene, . .	$C_{10}H_7\text{-}\alpha\text{-}CH_3$	—20°	240–243°.
β-Methyl-naphthalene, . .	$C_{10}H_7\text{-}\beta\text{-}CH_3$	+32.5°	241–242° (B. **25**, R. 857).
1,4-Dimethyl-naphthalene,	$C_{10}H_6\text{-}1,4\text{-}(CH_3)_2$	liquid	262–264° (B. **28**, R. 619).
α-Ethyl-naphthalene, . .	$C_{10}H_7\text{-}\alpha\text{-}C_2H_5$	"	258°.
β-Ethyl-naphthalene, . . .	$C_{10}H_7\text{-}\beta\text{-}C_2H_5$	—19°	251°.
Butyl-naphthalene, .	$C_{10}H_7 . C_4H_9$	. .	280° (B. **27**, 1623).
α-Phenyl-naphthalene, . .	$C_{10}H_7\text{-}\alpha\text{-}C_6H_5$	0°	325°.
β-Phenyl-naphthalene, . .	$C_{10}H_7\text{-}\beta\text{-}C_6H_5$	102°	347°.

α- and β-Phenyl-naphthalenes have been prepared by the action of diazobenzene chloride upon naphthalene in the presence of Al_2Cl_6.

Similarly, *nitrophenylnaphthalene*, melting at 129°, is obtained from sodium nitrophenylnitrosamine with naphthalene (B. **29**, 168; see also p. 106).

β-Phenylnaphthalene is also formed on conducting the vapors of brombenzene and naphthalene through tubes heated to redness; also in the condensation of two molecules of phenyl glycol (p. 391) (B. **26**, 1119, 1748), and in the distillation of β-phenylhydroxy-α-naphthoquinone with zinc-dust (A. **296**, 28). The constitution of the two isomeric phenylnaphthalenes can be deduced from their oxidation products: α-phenylnaphthalene yields o-benzoyl-benzoic acid, whereas β-phenyl-naphthalene yields phenyl-α-naphthoquinone:

$$C_6H_4\left\langle\begin{array}{l}CH{=\!=}CH\\ C(C_6H_5){=}CH\end{array}\right. \rightarrow C_6H_4\left\langle\begin{array}{l}COOH\\ CO.C_6H_5\end{array}\right. ; \quad C_6H_4\left\langle\begin{array}{l}CH{=}CH\\ CH{=}C.C_6H_5\end{array}\right. \rightarrow C_6H_4\left\langle\begin{array}{l}CO{-}CH\\ CO{-}C.C_6H_5\end{array}\right.$$

o-Phenylnaphthalene — o-Benzoyl-benzoic Acid — β-Phenylnaphthalene — Phenyl-α-naphthoquinone.

SUBSTITUTED NAPHTHALENES.

1. **Halogen Derivatives.**—These are formed (1) by the direct substitution of the hydrogen atoms by halogens; (2) by the replacement of NH_2-groups in amidonaphthalenes by halogens, following Griess' reaction (p. 58); (3) by the replacement of OH- as well as of SO_3H- and NO_2-groups in oxy-, nitro-, or sulpho-derivatives of naphthalene on heating them with PCl_5.

The union of the halogen atoms, and also that of the other substituents, like NO_2, SO_3H (compare B. **26**, 3028), in naphthalene derivatives are, as a rule, less stable than in the corresponding benzene derivatives.

Fluor-naphthalenes, $C_{10}H_7F$: the α-form boils at 216°, the β- melts at 59° and boils at 213°.

Chlor-naphthalenes, $C_{10}H_7Cl$: the α- boils at 263°, while the β- melts at 56° and boils at 265°. α-Chlornaphthalene is produced (1) in chlorinating boiling naphthalene; further, (2) by action of alcoholic potash upon naphthalene dichloride; (3) from naphthalene-α-sulphonic acid and PCl_5; (4) from α-amidonaphthalene. β-Chlornaphthalene is prepared from β-amidonaphthalene or from β-naphthol. **Dichlor-naphthalenes**: $C_{10}H_6Cl_2$. The ten possible isomerides are known: 1,2- melts at 35° and boils at 281°; 1,3- *melts at* 61° *and boils at* 289°; 1,4- *melts at* 68° *and boils at* 287°; 1,5- melts at 107°; 1,6- melts at 48°; 1,7- melts at 62° and boils at 286°; 1,8- melts at 83°; 2,3- melts at 120°; 2,6- melts at 135° and boils at 285°; 2,7- melts at 114° (B. **24**, 3475, R. 653, 704, 709; **26**, R. 536).

Trichlornaphthalenes.—There are fourteen isomerides—see B. **29**, R. 227.

Pentachlornaphthalene, $C_{10}H_3Cl_5$, melts at 168°. **Perchlornaphthalene**, $C_{10}Cl_8$, melts at 203° and boils at 403°.

Brom-naphthalenes, $C_{10}H_7Br$: the α-variety melts at 5° and boils at 279°, while the β-variety melts at 59° and boils at 282°. **Iodnaphthalenes**, $C_{10}H_7I$: the α-body is an oil, boiling at 305°; the β-body melts at 54.5°. α-Iodnaphthalene is obtained by the introduction of iodine into a carbon bisulphide solution of mercury dinaphthyl, $Hg(C_{10}H_7)_2$. See B. **29**, 1408, for the brom-iod-naphthalenes, and B. **27**, 599, for the **naphthyl-iodo-chlorides and iodosonaphthalenes.** Consult B. **29**, 1573, for **β-iodo-naphthalene.**

2. **Nitronaphthalenes**: **α-Nitronaphthalene**, $C_{10}H_7$-α-NO_2, consists of yellow needles, melting at 61° and boiling at 304°. It is produced on treating naphthalene with *nitric acid* at the ordinary temperature. When heated with PCl_5 it yields α-chlornaphthalene. Chromic acid oxidizes it to v-nitrophthalic acid. See p. 408 for the action of potassium permanganate. **β-Nitronaphthalene**, melting at 79°, is derived from β-nitronaphthylamine by replacing the NH_2-group by hydrogen, or better, from β-diazo-

naphthalene nitrite, $C_{10}H_7N = N . O . NO$, by means of Cu_2O (B. **20**, 1494). Different **dinitronaphthalenes** are obtained by the nitration of naphthalene at high temperatures. Consult B. **29**, 1243, 1521, for the separation of the 1,5 and 1,8-compounds. The 1,5-(α-) compound melts at 216°; the 1,8-(β-) body melts at 170°, and when heated with potassium cyanide yields potassium *naphthocyaminate*, $C_{28}H_{17}N_8O_9K$. The two dinitronaphthalenes, when heated with sulphuric acid and reducing agents, form *naphthazarin* or dioxynaphthoquinone (B. **27**, R. 959). 1,3-(γ-)-**Dinitronaphthalene**, melting at 144°, is obtained from amidodinitronaphthalene. At very low temperatures (—50 to —55°) nitric acid and naphthalene form various dinitronaphthalenes (B. **26**, R. 362). When naphthalene or dinitronaphthalenes are boiled for some time with fuming nitric and sulphuric acids (B. **28**, 367) **tri-** and **tetranitronaphthalenes** are produced. These explode partly with violence on heating.

3. **Nitrosonaphthalenes**: **Mononitrosonaphthalene**, $C_{10}H_7 . NO$, melting at 89° and decomposing at 134°, results from the action of nitrosyl bromide upon mercury dinaphthyl.

1,4-**Dinitrosonaphthalene** is a powder exploding at 120° and is produced when α-naphthoquinone dioxime (p. 406) is oxidized with red prussiate of potash. 1,2-**Dinitrosonaphthalene**, melting at 127° (B. **19**, 349; **21**, 434), is similarly formed from β-naphthoquinone dioxime.

4. **Amidonaphthalenes, Naphthylamines.**—(a) *Primary amines:* The naphthylamines, in contrast to the anilines, are very easily obtained by heating the oxynaphthalenes or naphthols with ammonia-zinc chloride (p. 72).

α-**Naphthylamine**, $C_{10}H_7$-α-NH_2, melting at 50° and boiling at 300°, results from the reduction of α-nitronaphthalene, or on heating α-naphthol with $ZnCl_2$ or $CaCl_2$-ammonia to 250°, and is synthetically produced when aniline and zinc chloride are heated with pyromucic acid. It crystallizes in flat needles, which are especially beautiful when they separate from aniline. It acquires a red color on exposure to the air, sublimes readily and possesses a pungent odor. In general, it deports itself perfectly similar to the phenylamines (compare p. 71).

Sodium in amyl alcohol reduces it to α-tetrahydronaphthylamine (p. 411). It is oxidized to α-naphthoquinone when boiled with chromic acid. Oxidizing agents (chromic acid, ferric chloride, silver nitrate) produce an azure-blue precipitate in the solutions of its salts: *oxynaphthylamine*, $C_{10}H_9NO$ (A. **129**, 255).

β-**Naphthylamine**, melting at 112° and boiling at 294°, results from β-naphthol and $ZnCl_2$-ammonia. It is odorless and is not colored by ferric chloride and the like. Potassium permanganate oxidizes it to phthalic acid. β-Tetrahydronaphthylamine is formed by its reduction.

Secondary and tertiary naphthylamines: Naphthylalkylamines are formed, analogous to the alkyl anilines, from the naphthylamines with alkylogens, or upon heating the naphthylamine hydrochlorides with alcohols: α-**Naphthylmethylamine**, $C_{10}H_7NH . CH_3$, boils at 293°; α-**Naphthylethylamine** boils at 303°; β-**Naphthyldimethylamine**, $C_{10}H_7$-β-$N(CH_3)_2$, melts at 46° and boils at 305° (B. **13**, 2053). The **Phenylnaphthylamines**, $C_{10}H_7 . NH . C_6H_5$, are formed when the hydrochlorides of α- and β-naphthylamines are heated with aniline and zinc chloride. On heating the naphthylamines with zinc chloride or with HCl to 180–190°, or with α- and β-naphthol various *dinaphthylamines* result. β,β-**Dinaphthylamine**, $C_{10}H_7$-β-NH-β-$C_{10}H_7$, melting at 171° and boiling at 471°, occurs as a by-product in the technical manufacture of β-naphthylamine. Heated to 150° with concentrated hydrochloric acid it breaks down into β-naphthylamine and β-naphthol. Heated with sulphur it forms thiodinaphthylamine, $NH(C_{10}H_6)_2S$, corresponding to thiodiphenylamine. When sulphuric acid

(80 per cent.) acts upon β-naphthylamine in the presence of oxidizing agents two naphthalene nuclei unite and *naphtidine* $(C_{10}H_6 . NH_2)_2$, results (B. **25**, R. 949) (p. 410).

The *acid derivatives of the naphthylamines* show great similarity to those of the anilines (see pp. 80–91). The **naphthyl benzene sulphamides**, $C_{10}H_7 . NH . SO_2 . C_6H_5$, manifest a rather remarkable deportment, similar to that of the naphthols, in that they dissolve in the alkalies, and unite similarly with diazo-salts, etc. (B. **27**, 2370). Consult B. **25**, R. 9, upon **naphthyl carbamine-chlorethyl esters**, $C_{10}H_7 . NH . COOC_2 . H_4Cl$, and their transposition products. See B. **29**, R. 184, for the α-naphthylamine derivatives of succinic, tartaric and citric acids.

Substituted Naphthylamines.—Haloid naphthylamines result by direct substitution, or by the action of ammonia upon substituted naphthols. 1,2- and 1,4-**Nitronaphthylamines** are formed by the nitration of acet-α-naphthylamine and its subsequent saponification. The 1,4-*body* melts at 191°. It is oxidized to α-naphthoquinone. It forms α-nitronaphthalene by the elimination of the NH_2-group. Boiling potassium hydroxide converts α-nitronaphthalene into 1,4-nitronaphthol (B. **19**, 796; **25**, R. 432). The 1,2-*compound* melts at 144°, and yields β-nitronaphthalene (p. 395) and 2,1-nitronaphthol (p. 401).

1-**Nitro-2-naphthylamine**, melting at 127°, is formed by the nitration of acet-β-naphthylamine and subsequent saponification of the acet-derivative. Nitrous acid and alcohol convert it into α-nitronaphthalene. 2,5- and 2,8-**Nitronaphthylamines** (B. **25**, 2076) are produced when β-naphthylamine nitrate is introduced into concentrated sulphuric acid.

Naphthylene Diamines.—*Diamidonaphthalenes, naphthylene diamines*, are obtained by the reduction of dinitro- and nitroamido-naphthalenes, also by the decomposition of amidoazo-naphthalenes, and when dioxynaphthalenes and amido-oxynaphthalenes are heated with ammonia (B. **21**, R. 839; **22**, R. 42; **26**, 188).

The o-naphthylene diamines adapt themselves like the o-phenylenediamines to condensation reactions, in that they form *naphtho-derivatives of heterocyclic rings* (see p. 95). To a certain degree the o-naphthylene diamines in this respect resemble the 1,8- or *peri*-compounds (p. 390).

1,2-**Naphthylene Diamine**, melting at 98°, is obtained by reduction from β-nitro-α-naphthylamine and β-naphthoquinone dioxime (p. 406). 2,3-**Naphthylene Diamine**, melting at 191°, is derived from 2,3-dioxynaphthalene by the action of ammonia at 240°. These two bodies yield **naphthoazimides** with nitrous acid, *anhydro* bases with carboxylic acids, *quinoxalines* with o-diketones, etc. (B. **25**, 2714; **26**, 188; **27**, 761). Perfectly similar hetero-ring formations are exhibited by 1,8- (Peri-) **naphthylene diamine**, melting at 67° and obtained from 1,8-dinitro- or 1,8-dioxynaphthalene; however, it does not, in contrast to the o-diamines, condense with o-diketones, like phenanthraquinones, forming **azines** (B. **22**, 861).

1,3-**Naphthylene Diamine** melts at 96° (B. **28**, 1953). 1,3-(m)-*Naphthylene diamine derivatives* are derived from naphthylamine sulphonic acids (p. 398), which contain the SO_3H group in the meta-position with reference to NH_2, by the action of amines.

(1,4)-**Naphthylene Diamine**, melting at 120°, results from the reduction of α-nitronaphthylamine, and the decomposition of α-amidoazo-naphthalene, by tin and hydrochloric acid. Ferric chloride converts it into α-naphthoquinone, and bleaching lime changes it to naphthoquinone dichlorimide.

See B. **25**, 2080, 2082, for 2,5- and 2,8-**naphthylene diamines**.

5. *Diazo- and Azo-compounds of naphthalene:* Nitrous acid (or sodium nitrite) acting upon naphthylamine salts produces naphthalene *diazo-derivatives* perfectly analogous to the diazo-benzene compounds (p. 99); they yield azo-dyes with the anilines and phenols. β-*Diazonaphthalic Acid*, $C_{10}H_7$-β $NHNO_2$ (p. 99), by rearrangement, yields 2-amido-1-nitronaphthalene (B. **30**, 1262).

The **azonaphthalenes** could not be prepared by reducing nitronaphthalenes.

α-**Azonaphthalene**, $C_{10}H_7N = N . C_{10}H_7$, results upon boiling the diazo-compound of amidazo-naphthalene with alcohol. It crystallizes in red needles, or small steel-blue prisms, melting at 190°, and subliming without difficulty. It dissolves with a blue color in concentrated sulphuric acid.

Benzene-azo-naphthalene, $C_{10}H_7 . N_2 . C_6H_5$, melting at 65°, has been similarly derived.

o-**Toluene-azo-naphthalene**, $C_{10}H_7 . N_2 . C_7H_7$, melts at 52° (B. **26**, 143).

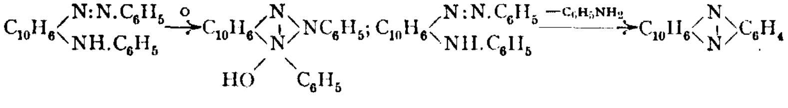
Naphthylazoacetic Ester, $C_{10}H_7 . N_2 . CH(COCH_3)CO_2R$, melting at 94°, is formed from diazonaphthalene chloride and sodium acetoacetic ester. Caustic potash changes it to naphthylacetone, and by the acid decomposition it is resolved into *naphthylazoacetic acid* (B. **24**, R. 571).

Amido azonaphthalenes: α-**Amido-azonaphthalene**, $C_{10}H_7$-α-N_2-α-$C_{10}H_6$ α_1-NH_2, melting at 175°, is formed by adding sodium nitrite (1 molecule) to the aqueous solution of naphthylamine hydrochloride (2 molecules); the diazo-amidonaphthalene, $C_{10}H_7 . N_2 . NH . C_{10}H_7$ (p. 107), first formed undergoes a molecular rearrangement. Tin and hydrochloric acid resolve α-amidoazonaphthalene into α-naphthylamine and (1,4)-naphthylene diamine. *Naphthalene Red* belongs to the safranine dyes and is produced when α-amidoazonaphthalene is heated with Na-naphthylamine hydrochloride.

β-**Amido-azo-naphthalene**, from β-naphthylamine, melts at 156° (B. **19**, 1282).

α-**Naphthylamine-azo-benzene Sulphonic Acid**, $C_6H_4(SO_3H) . N_2 . C_{10}H_6 . NH_2$, from sulphanilic acid and naphthylamine hydrochloride, is colored orange by caustic potash and *red* by acids (test for nitrous acid).

The o-azo-compounds of β naphthylalphylamines, like **Benzene-azo-β-naphthylphenylamine**, $C_{10}H_6\left\{\begin{matrix}[1]N:N.C_6H_5\\ [2]N:N.C_6H_5\end{matrix}\right.$, when oxidized form *ammonium bases* of the *pseudoazimide group*, and when heated they split off aniline, forming *naphthophenazines* (B. **28**, 328):



Compare further B. **18**, 3132; **20**, 1167; **24**, R. 765, *for the constitution* of the products resulting from the action of diazo-salts upon β-naphthylamines, which are sometimes viewed as β-quinone derivatives.

6. *Hydrazine Derivatives of Naphthalene:* **Hydrazonaphthalene**, $C_{10}H_7 . NH . NH . C_{10}H_7$, melting at 275°, corresponds to hydrazo-benzene. It is formed on boiling azonaphthalene with alcoholic sodium hydroxide and zinc-dust. When digested with hydrochloric acid it changes to the isomeric **Naphtidine** or diamido-dinaphthyl (compare benzidine, p. 118) (B. **18**, 3255).

Naphthyl Hydrazines, $C_{10}H_7 . NH . NH_2$, are derived from the diazo-chlorides of the two naphthylamines by the action of stannous chloride and hydrochloric acid (B. **19**, R. 303). The α-compound melts at 117°, the β-modification at 125°. They unite with the aldehydes and ketones forming hydrazones; these form naphthindol compounds by condensation, and manifest throughout the tendency to form derivatives and hetero-ring formations similar to those shown by the phenylhydrazines (pp. 123-129) (B. **19**, R. 831; **22**, R. 672).

7. **Sulphonic Acids.**—On digesting naphthalene with sulphuric acid we have formed α- and β **Naphthalene-sulphonic Acids.** At lower temperatures (80°) the α-acid, melting at 90°, predominates, while at about 160° and with an excess of sulphuric acid the β-acid, melting at 161°, is the chief product. When heated with sulphuric acid the α-acid passes into the β-variety. They may be separated by means of the calcium or lead salts. The free acids are crystalline and deliquesce readily. The α-acid decomposes upon heating with dilute hydrochloric acid to 200° into naphthalene and sulphuric acid, whereas the β-acid remains unaltered.

The *α-sulpho-chloride* melts at 66° and boils at 195° (13 mm.). The *β-sulpho-chloride* melts at 76° and boils at 201° (13 mm.) (J. pr. Ch. [2] **47**, 49). Protracted heating of naphthalene with concentrated sulphuric acid produces two isomeric disulpho-acids: 2,6- and 2,7-.

Naphthalene Disulphonic Acids.—They are separated by crystallizing their chlorides from benzene (B. **9**, 592). Additional disulphonic acids of naphthalene have been prepared by sulphonating the naphthalene monosulphonic acids, by oxidizing thionaphthol-sulphonic acids, from the naphthylamine disulphonic acids, etc. A series of **naphthalene trisulphonic acids** has been made by similar indirect methods (B. **24**, R. 654, 707,

715; 27, R. 81; Proc. 126, 168). **Chlor-naphthalene Sulphonic Acids** have been obtained in part by sulphonating the chlornaphthalenes, and in part by replacing the NH_2-group of the naphthylamine sulphonic acids by halogens (B. 24, R. 658, 707; 25, 2479; Ch. Z. 1895, 1114). **Nitronaphthalene Sulphonic Acids** are obtained by sulphonating the nitronaphthalenes or nitrating the chlorides of the sulphonic acids (B. 26, R. 536).

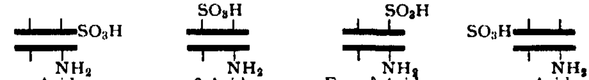
Some *naphthylamine sulphonic acids* possess technical value, inasmuch as they form desirable and valuable dyes by combining with the tetrazo-compounds of the benzidine series:

(*a*) α-Naphthylamine, treated at 130° with an excess of concentrated sulphuric acid, forms 1,4-**naphthylamine sulphonic acid, naphthionic acid,** which can also be prepared from nitronaphthalene with ammonium sulphite by simultaneous reduction and sulphonation (Ch. Z. 1895, 1114). The acid crystallizes with $\frac{1}{2}H_2O$ and dissolves sparingly in water. Its *sodium salt* has the formula $C_{10}H_6(NH_2)SO_3Na + 4H_2O$. When the acid combines with the tetrazo-derivative of benzidine *Congo red* is produced. Tin and hydrochloric acid decompose the latter with the formation of 1,2-*naphthylenediamine*-4-*sulphonic acid*. See B. **29**, 1978, for additional naphthylenediamine-sulphonic acids.

If α-naphthylamine be digested with sulphuric acid at 130° for some time there results, instead of the 1,4 acid, 1,5-**naphthylamine sulphonic acid**, *naphthalidinic acid*, and this finally gives place to the 1,6-acid (B. 26, R. 534). 1,8- or peri-**Naphthylamine Sulphonic Acid** is obtained from peri-nitrosulphonic acid. The derivatives of the 1,8-acid show a tendency to part with water with the production of *sultams*—*e.g.*:

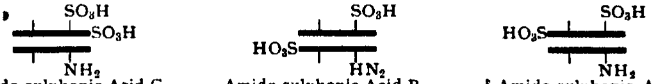
$(SO_3H)_2C_{10}H_4\left\langle\begin{matrix}SO_2\\ |\\ NH\end{matrix}\right.$, 1,8-**Naphsultam, 2,4-disulphonic Acid,** $(SO_3H)_3C_{10}H_3\left\langle\begin{matrix}SO_2\\ |\\ NH\end{matrix}\right.$, 1,8-**Naphsultamtrisulphonic Acid** (B. 27, 2137). Peri-Amidonaphthol derivatives are produced when these sultams are fused with caustic potash (B. 28, R. 636).

(*b*) Four different, isomeric *β-naphthylamine sulphonic acids* (A. **275**, 262) are produced, according to the temperature, when β-naphthylamine is sulphonated:



α-Acid (Baden Acid) | β-Acid (Brönner's Acid) | F- or δ-Acid | γ-Acid (Dahl's Acid).

These acids can also be prepared by the action of ammonia upon the corresponding naphtholsulphonic acids (p. 402). The β- and the F- or δ acids are particularly valuable, because by their combination with o-tetrazoditolyl beautiful red dyes having a blue tinge result. Certain *β-naphthylaminedisulphonic acids* are technically important:



Amido-sulphonic Acid G. (B. 24, R. 716) | Amido-sulphonic Acid R. (B. 24, R. 707) | δ-Amido-sulphonic Acid (B 24, R. 715).

See B. 27, 1193, for additional β-naphthylamidopolysulphonic acids. These β-naphthylamine sulphonic acids, which contain a sulpho-group in the m-position with reference to the NH_2-group, readily exchange the sulpho-group for the amine residue when they are heated with amines (B. 28, R. 311).

1,4-Diazonaphthalene Sulphonic Acid, $C_{10}H_6<\begin{smallmatrix}SO_2\\N_2\end{smallmatrix}>O$, *diazonaphthionic acid,* is produced by the action of nitrous acid upon naphthionic acid. It forms *rocellin* by combining with α-naphthol, and *azorubin* S by its union with α-naphthol-α-sulphonic acid.

By the union of various azonaphthalene diazo-sulphonic acids—*e. g.*, $C_{10}H_7N_2 . C_{10}H_5<\begin{smallmatrix}N_2\\SO_2\end{smallmatrix}>O$ — with naphthol-monosulphonic acid, azo-black dyes—*e. g.*, *naphthol-black*, *wool-black*, etc.—result.

8. *Naphthalene Sulphinic Acids* are derived by the reduction of the chlorides of sulpho-acids. **α-Naphthalene Sulphinic Acid,** $C_{10}H_7 . SO_2H$, melts at 84°, while the β-acid melts at 105° (B. **26**, R. 271). These acids behave just like the benzene sulphinic acids (p. 139) (B. **25**, 230). Mixed *naphthyl sulphones* are prepared from their salts by the action of alkyl bromides (B. **29**, R. 979).

9. **Naphthols:** The oxy-derivatives of naphthalene or naphthols in general show a deportment similar to that of the phenols. However, their hydroxyl-group is more reactive. They readily yield naphthylamines with ammonia. They form esters and ethers more easily than the phenols (B. **15**, 1427). The naphthols occur in coal-tar (A. **227**, 143).

α-Naphthol, $C_{10}H_7$-α-OH, melts at 95°, boils at 278–280°, and results from α-naphthylamine by means of the diazo-compound, and upon fusing α-naphthalene-sulphonic acid with alkalies. Its formation from phenylisocrotonic acid (p. 391) is very noteworthy. It is soluble with difficulty in hot water, readily in alcohol and ether, crystallizes in shining needles, has the odor of phenol, and is readily volatilized. Ferric chloride precipitates violet flakes of dinaphthol, $C_{20}H_{12}(OH_2)$, from its aqueous solution. Nitrous acid converts it into 2,1- and 4,1-nitrosonaphthol (p. 406); chlorine in acetic acid changes it to various chlorinated naphthols and ketohydronaphthalenes; potassium chlorate and hydrochloric acid oxidize it to dichlornaphthoquinone (A. **152**, 301); metallic sodium and alcohol reduce it to ar-tetrahydronaphthol (p. 412), while potassium permanganate in alkaline solution breaks it down into carbophenylglyoxylic acid (p. 392). The *acetate*, $C_{10}H_7$-α-O . C_2H_3O, melts at 46°. See B **28**, 3049, for the carbonate and phosphate.

β-Naphthol, $C_{10}H_7$-β-OH, melting at 122° and boiling at 286°, is derived from β-naphthalene-sulphonic acid, or β-naphthylamine. It is readily soluble in hot water and crystallizes in leaflets. Ferric chloride imparts a greenish color to the solution and separates a dinaphthol. Nitrous acid and β-naphthol yield 1,2-*nitrosonaphthol*. The *acetate*, $C_{10}H_7$-β-OC_2H_3O, melts at 70°.

The *bismuth salt* of β-naphthol has been recommended, under the name of *orpholum*, as an intestinal antiseptic.

Naphthol alkyl ethers are formed when the naphthols are heated with alcohols and hydrochloric acid to 150° (B. 15, 1427).

α-Naphthol Ethyl Ether boils at 277°. **β-Naphthol Methyl Ether** and **ethyl ether** have been called *Jara-Jara* and *Neroline* and been used in perfumery (B. **26**, 2706). α- and **β-Dinaphthyl Ethers** melt at 110° and 106° (B. **13**, 1840; **14**, 195).

Naphthol homologues, such as 2,1 and **3,1-methyl naphthol,** $C_{10}H_6(CH_3)OH$, melting at 80° and 92°, have been prepared from phenyl-α- and -β-methylisocrotonic acids (A. **255**, 272). **1,4-Dimethyl-3-naphthol,** $C_{10}H_5(CH_3)_2OH$, **melting at 136°, is obtained from** *santonin* (p. 432) (B. **28**, R. 116, 619).

Substituted Naphthols: Substituted α-naphthols can be synthesized from the substituted phenylisocrotonic acids (compare B. **26**, R. 537). Otherwise they are made by methods similar to those adopted with the substituted phenols (p. 148).

Nitronaphthols: 4,1-**Nitronaphthol**, $C_{10}H_6[4](NO_2)[1]OH$, melting at 164° and 2,1-**nitronaphthol**, $C_{10}H_6[2]NO_2[1]OH$, melting at 195°, result from the oxidation of 4,1- and 2,1-nitrosonaphthol with potassium ferricyanide or nitric acid (B. **25**, 973), or by boiling the corresponding nitronaphthylamines with caustic potash.

2,4-**Dinitro-α-naphthol**, melting at 138°, is produced by the action of nitric acid upon these nitro-naphthols or upon naphthalene-α-sulphonic acid, α-naphthylamine, and α-naphthol-disulphonic acid (A. **152**, 299). It is almost insoluble in water, sparingly soluble in alcohol and in ether, decomposes alkaline carbonates, and forms yellow salts with one equivalent of base. The salts dye silk a beautiful golden-yellow. The *sodium salt*, $C_{10}H_5(NO_2)_2 . ONa + H_2O$, finds use in dyeing, under the name of *naphthalene yellow* (Martius yellow), and is frequently used to color foods. The *potassium salt* of dinitro-naphthol-sulphonic acid, $C_{10}H_4(NO_2)_2\left\{\begin{matrix}[1]OK\\ [8]SO_3K\end{matrix}\right.$ (B. **24**, R. 709), obtained by the nitration of naphthol-trisulphonic acid, is *naphthol yellow*.

Trinitro-α-naphthol melts at 177°.

α-**Nitro-β-naphthol**, melting at 103°, is produced in the oxidation of α-nitroso-β-naphthol (p. 406), or from nitro-β-naphthylamine by the action of caustic potash. See B. **25**, 2079, R. 670, for other nitro-β-naphthols and -naphthol ethers.

Amido-naphthols: These are derived by the reduction of nitronaphthols, by the action of ammonia upon dioxy-naphthalenes, the decomposition of naphtholazo-comounds, etc., etc. In the isonuclear, particularly the 1,3-amidonaphthols, the NH_2-group is more readily displaced than in the hetero-nuclear isomerides.

(1,4)-**Amido-α-naphthol**, $C_{10}H_6(NH_2) . OH$, results from the reduction of (1,4)-nitronaphthol, and by the decomposition of α-naphthol orange, $C_{10}H_6(OH) . N_2 . C_6H_4 . SO_3H$. It is very unstable. It yields α-naphthoquinone by oxidation.

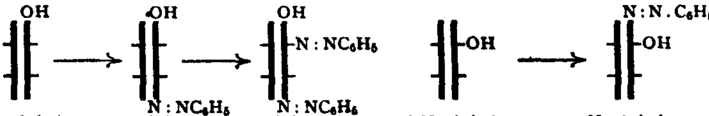
Its *ethyl ether*, $C_{10}H_6(OC_2H_5)NH_2$, melts at 96°. 4-*Acetamido-1-naphthol, naphthacetol*, melting at 187°, is especially well adapted for the production of pure naphtholazo-dyes (p. 402). 4-*Acetamino-1-naphthol Ethyl Ether, naphthacetin*, melts at 189° (B. **25**, 3059).

2-**Amido-α-naphthol**, from 2,1-nitronaphthol, oxidizes in the air to imido-oxynaphthylamine or β naphthoquinonimide, $C_{10}H_6\left\langle\begin{matrix}O\\ |\\ NH\end{matrix}\right.$, $C_{10}H_6\left\langle\begin{matrix}NH\\ O\end{matrix}\right.$, forming violet leaflets.

2,1-Amidonaphthol yields *anhydro bases* or *naphthoxazoles* (see p. 153 and B. **25**, 3430) with carboxylic acids, etc.

1-**Amido-β-naphthol**, from the reduction of 1-nitro- or nitroso-β-naphthol, or by the decomposition of β-naphthol orange, can be oxidized to β-naphthoquinone. 1,3-**Amido-naphthol** decomposes at 185° (B. **28**, 1952). 1,3-**Amido-naphthol** decomposes at 185° (B. **28**, 1952). 2,3-**Amido-naphthol**, melting at 234°, is produced by the action of concentrated ammonia at 135–140° (B. **27**, 763) upon 2,3-dioxynaphthalene.

Azonaphthols: The naphthols can be readily combined with all diazo-compounds to azo-derivatives. The α-naphthols add the diazo-group as easily to the para-(4-) as to the ortho (2-) position. However, the p-position is preferred and it is only when this is occupied that the o-position is assumed (B. **29**, 2945; **30**, 50). The final products are o,p-disazo-compounds. With the β-naphthols the diazo-group attaches itself only to the α-position referred to the OH-group:



α-Naphthol — 1-Naphthol-4-azobenzene — 1-Naphthol-2,4-disazobenzene, m. p. 193°, with decomposition — β-Naphthol — 2-Naphthol-1-azobenzene.

These same compounds are also obtained by the action of phenylhydrazine upon the *naphthoquinones* (p. 404). α-Naphthoquinone-phenylhydrazone is identical with 1-naphthol-4-azobenzene. β-Naphthoquinone and phenylhydrazine form a compound which probably is **1-naphthol-2-azobenzene**, melting at 128°, which cannot be directly made from α-naphthol, because it is converted by diazobenzene chloride into 1-naphthol-2,4-disazobenzene and in its other deportments justifies the assumption of the presence of an hydroxyl group (B. **24**, 1592; **28**, 2414).

The naphthol azo-dyes are of great importance in the color industry. They are prepared almost exclusively in the form of their sulpho-acids, which are formed (1) by the union of the naphthols with diazo-sulphonic acids—*e. g.*, **α-naphthol orange**, $OH[1]\text{-}C_{10}H_6[4].N_2.C_6H_4.SO_3H$, **$\beta$-naphthol orange**, $OH[2]C_{10}H_6[1]N_2C_6H_4SO_3H$, **rocellin**, $OH[2]C_{10}H_6[1]N_2.C_{10}H_6.SO_3H$, **Bieberich Scarlet**, $OH[2]C_{10}H_6[1]N_2.C_6H_3\text{-}(SO_3H)N_2.C_6H_4SO_3H$, form α- and β-naphthols with diazobenzene sulphonic acid, diazonaphthalene sulphonic acid, and sulphobenzeneazobenzene sulphonic acid; (2) by the combination of diazo-salts with naphtholsulphonic acids. Compare B. **29**, 2945, for the dyestuffs obtained from naphthacetol and diazo-compounds.

Amidonaphthols, together with amines, are obtained by the reduction of azonaphthols. The benzene azo-p-naphthol ethers, when reduced with $SnCl_2$, yield 2-*anilido*-1,4-*amidonaphthol ethers*, $C_{10}H_5(OR)(NH_2)(NHC_6H_5)$; the aniline residue enters consequently into the nucleus (B. **25**, 1013); compare semidine rearrangement (p. 118).

(d) *Naphthol sulphonic acids* have been made in great numbers and introduced into trade. In method of preparation and chemical behavior they exhibit nothing new, when compared with the phenol sulphonic acids (p. 156). In the following paragraph, therefore, a table alone of the representatives of these groups which possess a technical value will be introduced: *

α-Naphthol-mono-sulphonic Acids:

$C_{10}H_6OH.SO_3H$

OH	SO_3H	
1	2	Schaeffer's α-acid, A. **152**, 293.
1	3	B. **26**, R. 31.
1	4	Neville and Winther's acid, B. **24**, 3157; **27**, 3458; A. **273**, 102.
1	5	L-acid, A. **247**, 343.
1	7	B. **22**, 993.
1	8	Schöllkopf's acid, A. **247**, 306; B. **23**, 3088.

β-Naphthol-mono-sulphonic Acids:

$C_{10}H_6.OH.SO_3H$

OH	SO_3H	
2	6	Shaeffer's β-acid, A. **152**, 296.
2	8	*Croceïn Acid*, B. **22**, 453; **24**, R. 654.
2	5	γ-Mono-sulphonic Acid, B. **22**, R. 336.
2	7	F- or δ-acid (compare p. 319), B. **20**, 1426; **22**, 724.

α-Naphthol-disulphonic Acids:

$C_{10}H_5OH.SO_3H.SO_3H$

OH	SO_3H	SO_3H	
1	2	4	Disulphonic Acid for Martius' yellow, p. 401.
1	2	7	B. **25**, 1400.
1	3	8	ϵ-Disulphonic Acid, B. **22**, 3227.
1	4	6	D. R. P. 41957.
1	4	7	B. **24**, R. 709; **29**, 38.
1	4	3	Disulphonic Acid, S, B. **23**, 3090.

β-Naphthol-disulphonic Acids:

$C_{10}H_5OH.SO_3H.SO_3H$

OH	SO_3H	SO_3H	
2	3	6	**R-acid**, B. **22**, 396.
2	3	7	δ-Disulphonic Acid, B. **20**, 2906.
2	4	8	Disulphonic Acid, C, B. **26**, R. 259.
2	6	8	**G-acid**, B. **24**, R. 707.

* Compare Nietzki, "Organische Farbstoffe."

α-Naphthol-trisulphonic Acids:	*β-Naphthol-trisulphonic Acids:*
$C_{10}H_4OH \, . \, SO_3H \, . \, SO_3H \, . \, SO_3H$	$C_{10}H_4OH \, . \, SO_3H \, . \, SO_3H \, . \, SO_3H$
1 2 4 7 Sulphonic acid for *naphthol yellow* (p. 401).	2 3 6 8 B. 16, 462.
1 3 6 8 Sulphonic acid for *Chromotrope*, B. 24, R. 485.	(Consult B. 27, 1207, 1209, for other β-naphthol-trisulphonic acids.)

It is the acid of Neville and Winther—of all these acids—which is principally used in the making of azo-dyes. It corresponds to naphthionic acid. It is obtained in its present state by the action of concentrated sulphuric acid upon α-naphthyl carbonate. The R-acid and G-acid also meet with application. They unite with benzene and naphthalene diazo-salts to form a series of *Ponceau-* and *Bordeaux*-dyes of the most varying hues The most important sulphonic acids of β naphthol are produced together or one after the other in the sulphonation of β-naphthol in the manner represented in the following diagram:

	Schaeffer's β-Acid	R-Acid	
[2]-β-Naphthol ⟶	⟶ 2,6	⟶ 2,3,6	⟶ 2,3,6,8
	⟶ 2,8	⟶ 2,6,8	
	Croceïn Acid	G-Acid.	

The naphthol sulphonic acids containing an OH- and SO_3H-group in the 1,8- or peri-position give rise to anhydrides having a lactone nature; these are the *sultones* (compare sultams, p. 399).

Naphsultone, $C_{10}H_6 \left\{ \begin{array}{l} [1]O \\ [8]SO_2 \end{array} \right.$, melting at 154° and boiling above 360°, is formed by decomposing the diazo-derivative of peri-naphthylamine sulphonic acid. The sultone dissolves in hot alkalies forming salts of perinaphtholsulphonic acid. Sultones have also been obtained from 1,3,8- and 1,4,8-naphtholdi- and 1,3,6,8-trisulphonic acids.

Amidonaphtholsulphonic Acids are produced in the decomposition, by reduction, of the azo-derivatives of naphthol-sulphonic acids, and from nitrosonaphthols by reduction and sulphonation, both of which processes can be worked in common if the nitrosonaphthols be treated with sulphurous acid (B. 27, 23, 3050). In this way 1,2-nitrosonaphthol yields **1,2,4-amidonaphtholsulphonic acid,** $C_{10}H_5[1]NH_2[2]OH[4]SO_3H$. The isomeric 2,1,4-acid, $C_{10}H_5[1]OH[2]NH_2[4]SO_3H$, produces, even when oxidized in the air, *imido-oxynaphthalene-sulphonic acid*, $SO_3H \, . \, C_{10}H_5 \langle \begin{array}{l} O \\ | \\ NH \end{array}$. This dye is black-violet in color and is fast to light and alkalies (B. 25, 1400; 26, 1279). The 2,1,6-*acid*, $C_{10}H_5$-$[1]OH[2]NH_2[6]SO_3H$, is used as a photographic developer under the name of *Eikonogen*. Important dyes, from the technical point of view, are 2-amido-8-naphthol-6-sulphonic acids G (B. 25, R. 830; 29, 2267) and 1-amido-8-naphthol-3,6-disulphonic acid H (B. 26, R. 460, 917).

Dioxynaphthalenes.—Nine of the ten possible isomerides are known. The hydronaphthoquinones resulting from the reduction of the naphthoquinones are worthy of mention:

β-Hydronaphthoquinone, $C_{10}H_6[1,2](OH)_2$, melting at 60°, separates when a solution of β-naphthoquinone is boiled with sulphurous acid. It is strongly corrosive. It dissolves in the alkalies with a yellow color, which becomes an intense green upon exposure.

α-Hydronaphthoquinone, $C_{10}H_6[1,4](OH)_2$, melting at 173°, is obtained from α-naphthoquinone on boiling with hydriodic acid and phosphorus, or with zinc and hydrochloric acid. Chromic acid readily oxidizes it to α-naphthoquinone.

2,3-**Dioxynaphthalene** melts at 216° (B. **27**, 762). Also compare A. **247**, 356; B. **23**, 519, etc.

1,3-**Dioxynaphthalene,** *naphthoresorcinol,* melting at 124°, is obtained from 1,3,4-amidonaphtholsulphonic acid. It yields o-toluic acid when fused with caustic potash (see p. 195 and B. **29**, 1611).

2-*Phenyl*-1,3-*dioxynaphthalene,* melting at 166°, is made by the action of concentrated sulphuric acid upon α,γ-diphenylacetoacetic ester (p. 391). It absorbs oxygen and changes readily to phenylhydroxy-α-naphthoquinone. 1,7-*Dioxynaphthalene* melts at 175°; see B. **29**, 40; 2,7-*Dioxynaphthalene,* see B. **30**, 1119.

Trioxynaphthalenes.—Two trioxynaphthalenes, α- and β-**Hydrojuglones,** occur in green walnut shells of *Juglans regia* (B. **18**, 463, 2567). α-**Hydrojuglone,** $C_{10}H_5$-[1,4,5]$(OH)_3$, melting at 169°, is produced by the reduction of juglone. In the air it rapidly oxidizes to juglone. If it be distilled it changes to β-**Hydrojuglone,** melting at 97°, which does not yield juglone upon oxidation. It reverts again to α-hydrojuglone when boiled with dilute alcoholic hydrochloric acid.

1,2,5,6,-*Tetraoxynaphthalene,* melting at 154°, has been prepared by the reduction of naphthazarine (B. **28**, R. 543).

Thionaphthols have been prepared by the reduction of the chlorides of naphthalene sulphonic acids or from diazonaphthalenes (compare pp. 104, 156). **Thionaphthol,** *naphthyl mercaptan,* $C_{10}H_7 . SH$; the α-form is liquid and boils at 286°. The β-variety melts at 81° and boils at 286° (B. **22**, 821; **23**, R. 327). **Phenyl-β-naphthyl Sulphide,** melting at 51° (B. **24**, 2266), is formed when the *lead salt,* $(C_{10}H_7\text{-}\beta\text{-}S)_2Pb$, is heated, together with brombenzene. Different **dinaphthyl sulphides** have been prepared by heating the naphthyl-lead-mercaptides. Other methods have been employed in making them (B. **26**, 2816). Sulphur chloride and β-naphthol yield **dioxydinaphthyl sulphide,** $S(C_{10}H_6 . OH)_2$, melting at 211°. This can be readily oxidized to a *dehydro-compound*: $S\!<\!\begin{array}{l}C_{10}H_6O\\ |\\ C_{10}H_6O\end{array}$ (B. **27**, 2993; **28**, 114) (compare quinones with two nuclei, p. 339). **Naphthalene disulphydrates,** $C_{10}H_6(SH)_2$; see B. **25**, 2735.

(10) **Quinones**: 1,4- or α-Naphthoquinone corresponds to benzo-para-quinone, while 1,2- or β-naphthoquinone corresponds to the ortho-quinone of the benzene series, which is only known in certain derivatives. The same views as those indicated on p. 167 for benzoquinone argue for the constitution of the 1,4- or α-quinones.

α-Naphthoquinone, $O = [1]C_{10}H_6[4] = O$ or $\overline{O[1]C_{10}H_6[4]O}$, melting at 125°, crystallizes from alcohol in yellow plates, subliming under 100°. It possesses the usual quinone odor and is very volatile in a current of steam. It is formed (1) by oxidizing naphthalene in glacial acetic acid solution with chromic acid; (2) in the oxidation of 1,4-diamido- or 1,4-dioxynaphthalene, 1,4-amido-naphthol (A. **286**, 70), α-naphthylamine, etc., with sodium bichromate and sulphuric acid (B. **20**, 2283), and (3) when benzeneazonaphthol is treated in the cold with PbO_2 and sulphuric acid it is decomposed into diazobenzene sulphate and α-naphthoquinone (B. **24**, R. 733).

Nitric acid oxidizes α-naphthoquinone to phthalic acid, while α-hydronaphthoquinone is produced in its reduction. See the nitrogen quinone derivatives (p. 406) for its phenylhydrazine and hydroxylamine derivatives.

Substituted α-Naphthoquinones.—α-Naphthoquinone takes up two atoms of chlorine or bromine; the addition products readily part with hydrochloric and hydrobromic acids and become **β-Chlor- and β-Brom-α-naphthoquinones, melting at 117° and 130°.**

Hypochlorous acid converts a-naphthoquinone into *diketotetrahydronaphthylene oxide*, $C_6H_4\left\langle\begin{matrix}CO-CH\\ CO-CH\end{matrix}\right\rangle O$, which, by the breaking-down of the ethylene oxide union, readily takes up the elements of water, hydrogen chloride and $NH_2C_6H_5$. The primary addition products sustain the most varied transpositions with great readiness, and form: *oxynaphthoquinone, chloroxynaphthoquinone, anilido-oxynaphthoquinone, oxynaphthoquinone anil*, and other bodies; compare B. **25**, 3599.

Amido-derivatives.—Alkyl- or alphylamidonaphthoquinones are produced on heating primary amines together with α-naphthoquinone: **2-Anilido-α-naphthoquinone**, $C_{10}H_5O_2[2]NH . C_6H_5$, consists of red needles, melting at 191°. **2-Amido-α-naphthoquinone**, melting at 203°, is formed together with the isomeric oxy-α-naphthoquinone-imide on boiling amido-α-naphthoquinone-imide (p. 407) with water (B. **27**, 3337; B. **28**, 348).

Oxynaphthoquinones.—**2-Oxy-α-naphthoquinone**, *naphthalic acid*, $C_{10}H_5O_2[2]OH$, melting at 188°, is produced when anilido-naphthoquinone (see above) is boiled with dilute sodium hydroxide or oxynaphthoquinone anil (p. 407) with alcohol and sulphuric acid. **β-Phenyl-β_1-oxy-α-naphthoquinone**, melting at 147°, is prepared from β-phenyl-1,3-dioxynaphthalene by oxidizing it in alkaline solution with air (A. **296**, 18). **Iod-oxynaphthoquinone**, *Iod-naphthalic acid*, $C_{10}H_4O_2[2]OH[3]I$, results from the iodation of naphthalic acid (B. **28**, 348). Dyes of the *paroxazine*- and *paradiazine*-series are easily made from the o-oxy- and o-amidonaphthoquinone derivatives (compare also the corresponding naphthoquinone anils p. 407) and o-diamines (B. **28**, 353).

5-Oxy-α-naphthoquinone, Juglone, consists of yellow needles, melting with decomposition about 150–155°. The best method to obtain it consists in oxidizing α-hydrojuglone with ferric chloride. It may be synthetically prepared by oxidizing (1,5)-dioxynaphthalene with chromic acid (B. **20**, 934). It dissolves in alkalies with a violet color. Nitric acid converts it into dinitro-oxyphthalic acid (*juglonic acid*) (B. **19**, 164).

Oxy-juglone, *Dioxy-a-naphthoquinone*, melting with decomposition at 220°, is produced by the oxidation of the alkaline solution of juglone on exposure to the air. An isomeric **5,6-Dioxy-α-naphthoquinone**, *naphthalizarine* or **naphthazarine**, is formed on heating various α-dinitronaphthalenes with concentrated sulphuric acid in the presence of reducing agents (B. **27**, 3462, R. 959; A. **286**, 26). It corresponds to alizarine (p. 427), which may be imagined to have arisen from naphthazarine by the addition of a benzene nucleus. It is a valuable *mordant dye*. *Isonaphthazarine* is probably a **2,3-Dioxy-α-naphthoquinone**. It is produced from β-naphthoquinone by the action of a little bleaching lime as well as when 2,3-oxyanilido-α-naphthoquinone (see above) is heated with bromine (B. **25**, 409, 3606). **Carminic acid**, the coloring substance of cochineal, is an homologous dioxynaphthoquinone. It can be viewed as *8-methyl-2,6-dioxy-α-naphthoquinone* (p. 433).

β-Naphthoquinone, $C_{10}H_6[1,2]O_2$, is produced on oxidizing β-amido-α-naphthol with ferric chloride (B. **17**, R. 531; **21**, 3472). It consists of red needles, which decompose at 115–120°. It is distinguished from the para-quinones by being odorless and non-volatile. It closely resembles anthraquinone, and especially phenanthraquinone (p. 425); like the latter, it must be considered an ortho-diketone: $C_6H_4\left\langle\begin{matrix}CH:CH\\ CO . CO\end{matrix}\right.$.

Like α-naphthoquinone, it can add two atoms of chlorine and bromine, and by the elimination of halogen hydrides **Chlor- and Brom-β-naphthoquinones** are formed. A little bleaching lime converts β-naphthoquinone into *isonaphthazarine* (together with various other products, A. **286**, 59). This is a dioxy-α-napthoquinone. Such a rearrangement of 4-oxy- or 4-amido-β-naphthoquinone derivatives into oxy-α-naphthoquinone compounds is a phenomenon that has been frequently observed (compare oxy-α-naphthoquinone anil, p. 407). An excess of bleaching lime will produce a rupture in the ring of β-naphthoquinone and convert it into the lactone of o-phenylglycerol carboxylic acid (p. 393).

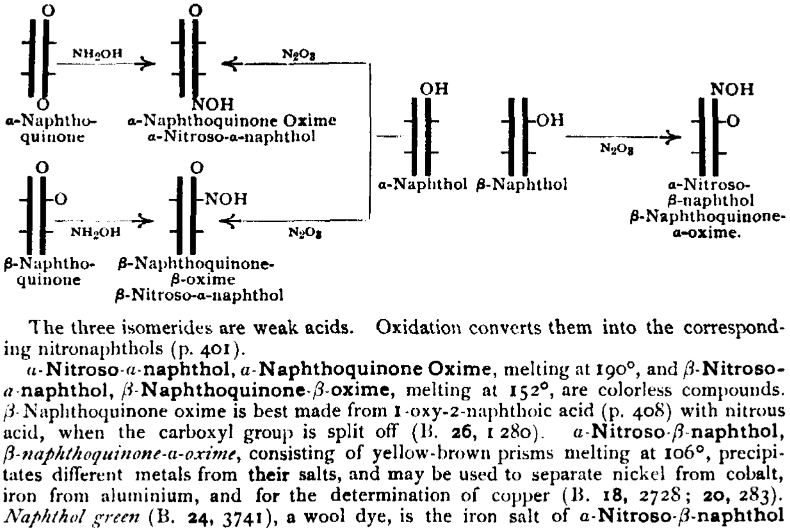
Similarly, 3-**Nitro-1,2-naphthoquinone**, melting at 158° and obtained by the nitration of β-naphthoquinone, is changed, on treating it with chlorine and water, into o-diderivatives of benzene.

3,4-**Dichlor-1,2-naphthoquinone**, on the contrary, is first rearranged by alkalies into dichlor-indene-oxy-carboxylic acid (p. 393). Potassium permanganate oxidizes β-naphthoquinone to phthalic acid, while sulphurous acid reduces it to β-naphthohydroquinone (p. 403), and hydriodic acid to β-naphthol (B. **26**, R. 586).

Nitrogen Derivatives of the Naphthoquinones.

(1) *Naphthoquinone Phenylhydrazones*: Unlike the benzene quinones (p. 160), both the α- and β-naphthoquinones unite with phenylhydrazine and form *phenylhydrazones* (B. **28**, 2414), which are, however, to be viewed rather as *azo-naphthols*.

(2) **Nitrosonaphthols or Naphthoquinoximes.**—These are produced when the alcoholic solutions of the α- and β-naphthoquinones are boiled with hydroxylamine hydrochloride, and by the action of nitrous acid upon the naphthols, hence they can be regarded as nitrosonaphthols, $C_{10}H_6(O)(NOH)$ or $C_{10}H_6(OH)(NO)$ (compare nitrosophenols, p. 151). Three isomeric bodies are formed; their relation is expressed by the following diagram:



The three isomerides are weak acids. Oxidation converts them into the corresponding nitronaphthols (p. 401).

α-**Nitroso-α-naphthol, α-Naphthoquinone Oxime**, melting at 190°, and β-**Nitroso-α-naphthol, β-Naphthoquinone-β-oxime**, melting at 152°, are colorless compounds. β-Naphthoquinone oxime is best made from 1-oxy-2-naphthoic acid (p. 408) with nitrous acid, when the carboxyl group is split off (B. **26**, 1280). α-**Nitroso-β-naphthol**, *β-naphthoquinone-α-oxime*, consisting of yellow-brown prisms melting at 106°, precipitates different metals from their salts, and may be used to separate nickel from cobalt, iron from aluminium, and for the determination of copper (B. **18**, 2728; **20**, 283). *Naphthol green* (B. **24**, 3741), a wool dye, is the iron salt of α-**Nitroso-β-naphthol Sulphonic Acid**, $C_{10}H_5(SO_3H)O(NOH)$, obtained by the action of nitrous acid upon Schaeffer's β-naphthol sulphonic acid (p. 402). Consult B. **30**, 187, for the product obtained in the action of NO_2-vapors upon Schaeffer's β-acid.

The *ethers* of the nitroso-naphthols, derived from the silver salts with methyl iodide and partly from the quinones with alkylhydroxylamines, are reduced to amidonaphthols by tin chloride (B. **18**, 715, 2225), a proof of the "oxime formula" of the nitrosonaphthols.

α-**Naphthoquinone Dioxime**, $C_{10}H_6\text{-}1,4\text{-}\begin{cases}N.OH\\N.OH\end{cases}$, is formed from α-nitroso-α-naphthol with hydroxylamine hydrochloride. It melts at 207° (B. **21**, 433).

β-**Naphthoquinone Dioxime**, $C_{10}H_6\text{-}1,2\text{-}\begin{cases}N.OH\\N.OH\end{cases}$, is derived from β-nitroso-α-naphthol and from α-nitroso-β-naphthol by the action of hydroxylamine hydrochloride (B. **17**, 2064, 2582). It melts at 149°. After the manner of the glyoximes it forms the *anhydride*, $C_{10}H_6\begin{cases}[1]N\\[2]N\end{cases}\!\!>O$, melting at 78°, when digested with alkalies. This com-

pound may also be designated *naphtho-furazane.* The reduction of the dioximes gives rise to naphthylenediamine.

(3) *Naphthoquinone Chlorimides* (p. 172): These are made from amido-naphthols, and the dichlorimides from the naphthylene diamines with a bleaching lime solution (B. 27, 238). They resemble the benzoquinone chlorimides, but do not exhibit the same dye-stuff condensations as the former (B. 27, 242).

α-Naphthoquinone Chlorimide, $C_{10}H_6[1,4](NCl)O$, melts at 109°.
α-Naphthoquinone Dichlorimide, $C_{10}H_6[1,4](NCl)_2$, melts at 137°.

β-Naphthoquinone-α-chlorimide, melting at 87°, and **β-Naphthoquinone-β-chlorimide,** decomposing at 98°, are derived from 2,1- and 1,2-amidonaphthols; they yield β,α- and α,β-nitrosonaphthols with hydroxylamine. **β-Naphthoquinone dichlorimide** melts at 105°.

(4) *Naphthoquinone-imides and Anils:* The indophenol and indo-aniline dyes of the naphthalene series belong in this group,—*e. g.*, **α-Naphthol Blue** or **Indophenol,** $C_{10}H_6[1]O[4]N.C_6H_4N(CH_3)_2$,—which results when naphthol interacts with dimethyl-p-phenylenediamine or nitrosodimethyl aniline. The simple α-naphthoquinone-imide is not known. **2-Amido-1,4-naphthoquinone-imide,** *diimidonaphthol,* $C_{10}H_5[2]NH_2$-$[1]O[4]NH$ (A. 154, 303), is produced in the oxidation of 1-oxy-2,4-diamidonaphthalene. Boiling water changes diimidonaphthol to **2-oxy-1,4-naphthoquinone-imide,** melting at 195° (B. 23, 2454); aniline to **2-anilido-1,4-naphthoquinone anil,** $C_{10}H_5$-$[2]NHC_6H_5[1]O[4]NC_6H_5$, melting at 187° (B. 13, 123; 21, 391, 676); with hydroxylamine an **oxynaphthoquinone oxime,** which consists of two modifications, red and yellow, which can be changed one into the other (B. 29, 1415). **2-Oxy-1,4-naphthoquinone anil,** melting at 240° with decomposition, is produced by the action of aniline in the cold upon β-naphthoquinone-4-sulphonic acid, the oxidation product of 1,2-amidonaphthol-4-sulphonic acid. This is an instance of the rearrangement of a β- into an α-naphthoquinone derivative. The p-diamines react in a manner similar to aniline, so that in this way hydroxyl indaniline dyes (see above) can be obtained (B. 27, 25, 3050).

α-Naphthoquinone-phenyldiimide, $C_{10}H_6(NH)(NC_6H_5)$, melting at 129°, is formed upon oxidizing p-amidonaphthylphenylamine with mercuric oxide (A. 286, 186).

β-Naphthoquinone-imides, also called *imido-oxy-* or *imidoketone naphthalenes,*—*e. g.*, $C_{10}H_6$-1,2-O(NH) (pp. 401, 403),—are produced when the alkaline solutions of the 1,2-amidonaphthols are oxidized with air.

II. ALCOHOLS OF THE NAPHTHALENE SERIES AND THEIR OXIDATION PRODUCTS.

A. *Alcohols:* **Naphthobenzyl Alcohols,** *Naphthyl Carbinols,* $C_{10}H_7.CH_2.OH$, the α- melting at 60° and boiling at 301°, and the β- melting at 80°, result when their amines are treated with nitrous acid (B. 21, 257). The **naphthobenzyl chlorides,** $C_{10}H_7CH_2Cl$, the α- boiling at 178° (25 mm.) and the β- melting at 47°, are formed when chlorine acts upon the two methyl naphthalenes (p. 394) at a boiling temperature (B. 24, 3928). **Naphthobenzylamines,** *menaphthylamines,* $C_{10}H_7.CH_2.NH_2$, the α-boiling at 292° and the β- melting at 60°, have been made by the reduction of the corresponding naphthoic acid thiamides, as well as of the naphthonitriles.

B. *Aldehydes, Ketones:* When the naphthyl-methyl alcohols are oxidized, the products are:

α-Naphthaldehyde, $C_{10}H_7.CHO$, boiling at 291°, and **β-Naphthaldehyde,** melting at 59° (B. 20, 1115; 22, 2148).

α-Naphthyl-methyl Ketone, *Acetonaphthone,* $C_{10}H_7.CO.CH_3$, is derived from naphthalene and acetyl chloride by means of aluminium chloride. It melts at 34° and boils about 295°. Its chloride splits off hydrogen chloride and becomes *α-naphthyl acetylene,* $C_{10}H_7.C{:}CH$. Potassium permanganate oxidizes the ketone to α-naphthyl glyoxylic acid, $C_{10}H_7CO.COOH$, melting at 113°, which is also formed by the saponification of naphthol cyanide obtained from α-naphthoyl chloride. By reduction it becomes *α-naphthyl acetic acid,* $C_{10}H_7.CH_2.COOH$, melting at 131°. **1-Naphthol-3-methyl Ketone,** $C_{10}H_6[1](OH)[3](CO.CH_3)$, melting at 174°, is formed from β-benzal-lævulinic acid by condensation (p. 391 and B. 24, 3201). See B. 28, 1946, for **1,2-naphthol methyl ketone.**

C. *Naphthalene Monocarboxylic Acids:*

α-**Naphthoic Acid,** $C_{10}H_7$-α-CO_2H, melting at 160°, is derived from α-naphthonitrile by saponification (B. **20,** 242; **21,** R. 834); by fusing α-naphthalene sulphonic acid with sodium formate; by the action of sodium on a mixture of α-brom-naphthalene and chlor-carbonic ester; and from naphthalene, urea chloride, and aluminium chloride (B. **23,** 1190). β-**Naphthoic Acid,** melting at 182°, is formed from β-naphthonitrile (B. **24,** R. 725), as well as by the oxidation of β-alkylnaphthalenes (B. **17,** 1527; **21,** R. 355). Both acids are decomposed when heated with baryta into CO_2 and naphthalene.

Homologous Naphthalene Carboxylic Acids: α-**Naphthyl-acetic Acid,** $C_{10}H_7$-α-$CH_2.COOH$, melting at 131°, has been made by the reduction of α-naphthyl glyoxylic acid (p. 407), while the β-*acid*, melting at 139°, has been prepared by means of the cyanide from β-naphthobenzyl chloride (B. **29,** 2373).

β-**Phenyl-** and β-**Naphthyl-α-naphthoic Acids** are the *chrysenic* and *picenic* acids (see chrysene and picene, p. 416).

Substituted Naphthoic Acids: The nitration of α-naphthoic acid produces 1,5- and 1,8-**nitronaphthoic acids,** melting at 239° and 275° respectively. Boiling nitric acid converts them into 1,5-(α-) and 1,8-(β) dinitronaphthalene (p. 396). 1,4-**Nitronaphthoic acid,** melting at 220°, results upon saponifying the nitrile, which is formed on treating the diazo-derivative of 1,4-nitronaphthylamine with potassium cuprous cyanide.

Ferrous sulphate and ammonia reduce the 1,5-acid to a stable **amido-naphthoic acid** (1,5)-, melting at 212° (B. **19,** 1981), whereas the same reagents reduce the 1,8-acid to (1,8)- or peri-**amido-naphthoic acid,** which when free, passes like the 1,8-amido-sulphonic acids (p. 399), quite readily into its inner anhydride, **Naphthostyril,** $C_{10}H_6\left\{\begin{matrix}[1]CO\\ [8]NH\end{matrix}\right.$, melting at 179° (B. **19,** 1131). 1,4-**Amidonaphthoic Acid** melts at 177° (B. **28,** 1842).

See B. **24,** R. 637, for the **nitro-β-naphthoic acids.** 2,3-**Amido-naphthoic Acid,** melting at 214°, results upon treating the corresponding oxy-naphthoic acid with ammonia (B. **28,** 3089).

Oxynaphthoic Acids, Naphthol Carboxylic Acids, containing the OH- and COOH-groups in the ortho-position, are prepared like the orthophenol carboxylic acids—*i. e.*, by heating the sodium naphtholates with CO_2 under pressure.

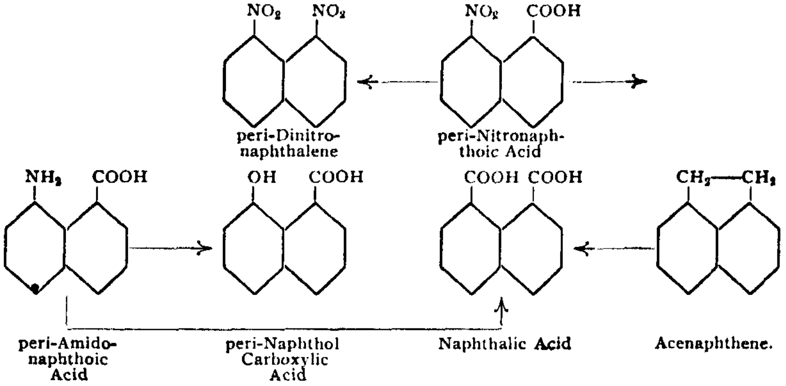
1,2-(α-) **Naphthol Carboxylic Acid,** $C_{10}H_6[1](OH)[2](COOH)$, melting at 186°, is formed from α-naphthol, and from β-naphthol-sodium with carbon dioxide and pressure at 120–145°; 2,1-(β)-**Naphthol Carboxylic Acid,** melting with decomposition at 156°, is similarly produced, while if β-naphthol-sodium be heated more strongly, 200–250°, in a current of carbon dioxide, the product will be 2,3-*naphthol carboxylic acid*, melting at 216°. The 2,1-(β)-naphthol carboxylic acid is distinguished by the easy mobility of its carboxyl group. Heated alone, or when boiled with water, it changes to β-naphthol; nitrous acid converts it into α-nitroso-β-naphthol (see p. 406 for method of preparation), and diazobenzene salts into benzene azo-β-naphthol, etc. The 2,3-acid, on the other hand, is very stable, and resembles salicylic acid. Because of its striking and remarkable yellow color the formula of a *ketodihydronaphthoic acid*, $C_6H_4\left<\begin{matrix}CH_2-CO\\ |\\ CH=C.COOH\end{matrix}\right.$, has been proposed for this acid. The behavior of the acid toward phenylhydrazine supports this view: it is very probable that at first a hydrazine is produced, which subsequently, owing to indol condensation, forms a phenonaphtho-carbazole-carboxylic acid (B. **29,** 265).

Naphthoxanthones, $C_{10}H_6<\begin{matrix}O\\ CO\end{matrix}>C_{10}H_6$ (B. **25,** 1642), are produced when the three o-naphthol carboxylic acids are heated with acetic anhydride.

(1,8)- or peri-**Naphthol Carboxylic Acid** is derived from (1,8)-amido-naphthoic acid by means of the diazo-compound. It breaks down into water and its γ-*lactone*, $C_{10}H_6\left\{\begin{matrix}[1]O\\ [8]CO\end{matrix}\right>$, melting at 169°.

2,3-Oxynaphthoic acid and diazobenzene chloride yield a mixed azo-compound. Reduction converts this into **1,2,3-amido-oxynaphthoic acid**, which, on boiling with sulphuric acid, becomes **1,2,3-dioxynaphthoic acid**. This can also be obtained from β-naphthohydroquinone and carbon dioxide, and by oxidation it is changed to **β-naphthoquinone-carboxylic acid** (B. **28**, 3089). Consult B. **29**, 39.

D. *Naphthalene Di- and Poly-carboxylic Acids:* Six of these acids are known. It is remarkable that the 1,8- or peri-acid, so-called **naphthalic acid**, $C_{10}H_6[1,8](COOH)_2$, is produced by the oxidation of acenaphthene (p. 410), and also from its *half-nitrile*, which is made by saponifying the diazo-derivative of peri-amidonaphthoic acid. The following diagram represents the relations of a series of *peri-naphthalene derivatives:*



Just as in the case of other peri-derivatives, so here naphthalic acid when heated to 180° breaks down without melting into water and its *anhydride*, $C_{10}H_6(CO)_2O$, melting at 266°, which like phthalic anhydride condenses with phenol to *phenol-naphthaleïn*, $C_{10}H_6\langle{}^{C(C_6H_4OH)_2}_{CO}\rangle O$ (B. **28**, R. 621). Compare B. **28**, 360, for naphthal-imide, -anil, and -phenylhydrazil. **1,2-Naphthalene Dicarboxylic Acid**, obtained by the saponification of its nitrile, melts at 175° and passes into its *anhydride*, melting at 105° (B. **25**, 2475). **1,5-Naphthalene Dicarboxylic Acid**, B. **29**, R. 516.

Naphthalene Tetracarboxylic Acid, $C_{10}H_4[1,4,5,8](CO_2H)_4$, with the carboxyl groups in the two peri-positions of naphthalene, results when pyrenic acid is oxidized (B. **20**, 365).

Naphthonitriles, Cyan-naphthalenes: Naphthonitriles may be obtained by the distillation of the alkali salts of the naphthalene-disulphonic acids, or the phosphoric esters of the naphthols with potassium cyanide or yellow prussiate of potash (B. **21**, R. 834).

α-Naphtho-nitrile, α-Cyan-naphthalene, $C_{10}H_7 . CN$, melting at 37° and boiling at 298°, has also been prepared from formnaphthalide, $C_{10}H_7 . NH . COH$, as well as from α-naphthalene diazochloride by means of copper and potassium cyanides.

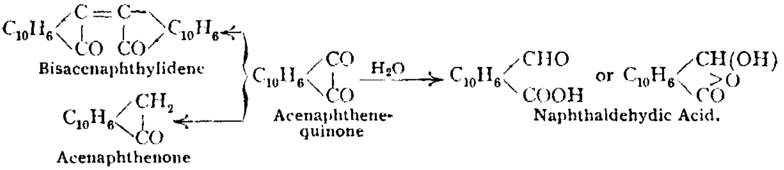
β-Cyan-naphthalene melts at 66° and boils at 304°. **1,2-Dicyan-naphthalene**, $C_{10}H_6[1,2](CN)_2$, melting at 190°, is produced when 1,2-chlornaphthalene sulphonic acid is distilled with potassium ferrocyanide (B. **25**, 2475). For additional isomeric dicyan-naphthalenes see A. **152**, 289; J. 1869, 483, etc.

12. **Dinaphthyl- and Dinaphyl-methane Derivatives**: Different isomeric **dinaphthyls** have been made by conducting the vapors of naphthylene through tubes heated to redness, by heating naphthalene with Al_2Cl_6, or from brom-naphthalene and sodium, and by heating mercury dinaphthyl, $Hg(C_{10}H_7)_2$, etc. (B. **28**, R. 184).

The **diamidodinaphthyls** or **naphtidines**, corresponding to the benzidines or diamidodiphenyls, result from the rearrangement of the hydrazonaphthalenes, or directly from the naphthylamines by the action of 80 per cent. sulphuric acid in presence of oxidants, such as ferric oxide, etc. (B. **25**, R. 949). Similarly, naphthols and ferric chloride yield **dinaphthols**.

Dinaphthylmethane derivatives, like α-**dinaphthol methane**, $CH_2(C_{10}H_6\text{-}\alpha\text{-}OH)_2$, and **ethidene-α-dinaphthol**, $CH_3 . CH(C_{10}H_6OH)_2$, have been made by the condensation of naphthols with aldehydes. The products from the latter and β-naphthol readily part with water and become *xanthenes*, hence they in all probability contain the alkylidene groups in the o-position with reference to the hydroxyls: β-**Dinaphthol methane**, melting at 190°, yields, with $POCl_3$, *dinaphthoxanthene*, $C_{10}H_6<{}^{O—}_{CH_2}>C_{10}H_6$, while benzaldehyde and β-naphthol at once form ms-*phenylnaphthoxanthene*, $C_6H_5CH(C_{10}H_6)O$ (B. **25**, 3477; **26**, 83), together with an acetal (see I, p. 200).

13. **Acenaphthene**: Acenaphthene, or peri-*Ethylene Naphthylene*, $C_{10}H_6\begin{cases}[1]CH_2\\ [8]CH_2\end{cases}$, melting at 95° and boiling at 277°, is a peculiar derivative of naphthalene, which is obtained by conducting α-ethyl naphthalene through a red-hot tube, or by the action of alcoholic potash upon *α-brom-ethyl naphthalene*, $C_{10}H_7 . C_2H_4Br$. It also occurs in coal tar. Inasmuch as acenaphthene is oxidized by sodium bichromate and sulphuric acid to naphthalic acid (p. 409) the side-chain C_2H_4 must be arranged in the two peri-positions (1 and 8) of naphthalene. **Acenaphthene-quinone**, $C_{10}H_6(CO)_2$, melting at 261°, is a by-product in this oxidation. Zinc-dust and acetic acid reduce it to **acenaphtenone**, $C_{10}H_6 . CH_2 . CO$, melting at 121°, while hydriodic acid and phosphorus change it to **bisacenaphthylidene**, $(C_{10}H_6 . CO . C:)_2$, melting at 294°, and alkalies decompose it into *naphthaldehydic acid* (B. **26**, R. 710; A. **290**, 195):



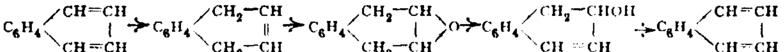
When the vapor of acenaphthene is conducted over lead oxide heated to redness two atoms of hydrogen split off and **acenaphthylene**, $C_{10}H_6\langle{}^{CH}_{CH}$, results. This forms *yellow* plates (p. 419) (B. **26**, 2354), melts at 92° and boils at 270° with decomposition. Chromic acid also oxidizes it to naphthalic acid.

14. Hydronaphthalene Derivatives.

Hydronaphthalene compounds attach themselves to naphthalene just as the hydroaromatic benzene derivatives did to benzene. Naphthalene and its derivatives take up hydrogen and the halogens more readily than the compounds of benzene. Those naphthalene derivatives which have added hydrogen to *one* nucleus alone are remarkable and interesting because they manifest in one substance the differences which prevail between an *aromatic* and a *hydroaromatic* or *alicyclic* nucleus. While the non-hydrogenized nucleus of the respective naphthalene compounds retains the aromatic properties, the hydrogenized *alicyclic* nucleus assumes, on the contrary, the nature of a fatty radical, and as a consequence the

whole system acquires the character of an homologous benzene derivative (Bamberger, A. 257, 1).

A. **Dihydronaphthalene Derivatives**: **Dihydronaphthalene**, $C_{10}H_{10}$, melting at 15° and boiling at 212°, is formed when naphthalene is reduced with sodium in a boiling ethyl alcohol solution. The entering hydrogen atoms assume the 1,4-position, because the hydride yields o-phenylene diacetic acid when it is oxidized. It can be viewed as the hydrocarbon of α-naphthoquinone if the latter be considered as a diketone. Dihydronaphthalene resembles the olefines—*e. g.*, ethylene—in that it readily takes up two univalent atoms or radicals. Thus with bromine it forms a *dibromide*, with hypochlorous acid a *glycolchlorhydrin* (p. 412). *Tetrahydronaphthylene oxide* (p. 412) can be easily obtained from the latter and is capable of rearranging itself to **1,2-dihydro-β-naphthol**, $C_{10}H_{10}O$, boiling at 162–168° (28 mm.), which may be oxidized to dihydroisocoumarin-carboxylic acid (p. 392), and when it splits off water naphthalene is produced (A. 288, 74):



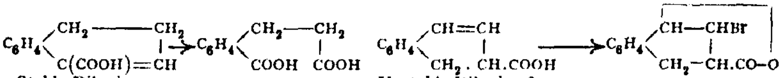
Naphthalene Dihydro-naphthalene Tetrahydro-naphthalene Oxide Dihydro-β-naphthol Naphthalene.

Naphthalene Dichloride, $C_{10}H_8Cl_2$, is a yellow oil formed when naphthalene is treated with potassium chlorate and hydrochloric acid. It changes to α-chlornaphthalene at 40–50°, and by the elimination of hydrogen chloride.

Dihydronaphthoic Acids: Sodium amalgam reduces the α- and β-naphthoic acids, two hydrogen atoms being added to the nucleus already carrying the carboxyl-group, and in the cold there result *unstable*, and when heat is applied *stable*, **dihydronaphthoic acids**, $C_{10}H_9 . CO_2H$:

α-Stable melting at 125°; β-stable melting at 161°.
α-Unstable " " 91°; β-unstable " " 104°.

The unstable pass into the stable modifications on boiling them with caustic soda. Potassium permanganate oxidizes the stable α-acid to hydrocinnamic acid, while the unstable acid yields oxalic acid and phthalic acid. The dibromide of the unstable β-acid, in contrast with the stable modification, readily changes to a brominated lactone. All these facts point to the following formulas for the stable α- and the unstable β-acid (A. 266, 169):



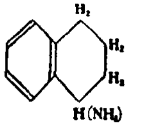
Stable Dihydro-α-naphthoic Acid Unstable Dihydro-β-naphthoic Acid.

The dihydro-β-acids, when oxidized with potassium ferricyanide, revert again to β-naphthoic acid.

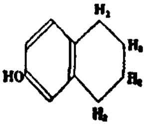
B. **Tetrahydronaphthalene Derivatives**: **Tetrahydronaphthalene**, $C_{10}H_{12}$, boiling at 206°, is formed in the reduction of naphthalene with sodium in amyl alcohol solution; also from ar-tetrahydronaphthylamine by the elimination of the NH_2-group; hence the H-atoms are only present in the one nucleus. **Naphthalene Tetrachloride**, $C_{10}H_8Cl_4$, melting at 182°, is produced when chlorine is conducted into a chloroform solution of naphthalene. Boiling alcoholic potash changes it to dichlornaphthalene (p. 395). See B. 28, R. 392, for the oxidation of naphthalene tetrachloride. Consult B. 24, R. 713, for the chlorine addition products of chlorinated and sulphur-containing naphthalenes. **Naphthalene Tetrabromide** melts at 111° (C. 1897, 1, 984).

The naphthylamine and naphthol hydrides are particularly interesting. Sodium acting upon the boiling amyl alcohol solution of the naphthols and naphthylamines causes these bodies to add four hydrogen atoms each to one nucleus. If the latter carries the NH_2- or OH-group, the body formed no longer possesses the character of a naphthylamine or a

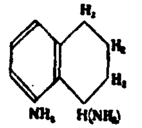
naphthol, but has that of a benzene homologue, amidated or bearing the OH-group in the side-chain. Should, however, the non-substituted nucleus be hydrogenized, then the products acquire the nature of homologous anilines or phenols. E. Bamberger, who first observed these relations and explained them, designated the second class of tetrahydro-derivatives as *aromatic* (ar-), and the first class as *aliphatic-cyclic* or *alicyclic* (ac-):



ac-Tetrahydro-α-naphthylamine



ar-Tetrahydro-β-naphthol



ar-, ac-Tetrahydro-1,5-naphthylene Diamine.

α-Naphthylamine and α-naphthol upon reduction yield ar-tetrahydro-α-naphthylamine and -naphthol, while the β-compounds form both the ar- and the ac-tetrahydro-derivative; the latter predominates. 1,5-Naphthylene diamine yields ac-, ar-tetrahydro-naphthylene diamine, which, by elimination of the aromatic NH_2-group, forms ac-tetrahydro-α-naphthylamine:

ar-**Tetrahydronaphthylamines**, $NH_2 . C_6H_3 : (C_4H_8)$. The α-body boils at 275° *and the β-form at 276°. They are feeble bases and form diazo- and azo-compounds.* They exercise a reducing power with salts of the noble metals. By oxidation with potassium permanganate all yield adipic acid and oxalic acid (p. 393).

Chromic acid oxidizes the α-compound to ar-**tetrahydro-α-naphthoquinone**, $C_6H_2O_2 : (C_4H_8)$, melting at 55°, which in every respect resembles benzoquinone—*e. g.*, like the latter, it does not form a hydrazone with phenylhydrazine (compare p. 406). ac-**Tetrahydronaphthylamines**, $C_6H_4 : (C_4H_7 . NH_2)$; the α-body boils at 246° and the β- at 249°. *They are strong bases, which absorb carbon dioxide from the air. They* do not form diazo-derivatives. Potassium permanganate ruptures the hydrogenized ring and produces o-cinnam-carboxylic acid.

ac-, ar-**Tetrahydro-1,5-naphthylene Diamine**, $NH_2 . C_6H_3 : (C_4H_7NH_2)$, melting at 77° and boiling at 261°, combines in itself both the properties of an aromatic and of an alicyclic amine. It contains an asymmetric carbon atom, and has been resolved into a dextro- and a lævo-modification.

ar-**Tetrahydro-α-naphthol**, $OH . C_6H_3 : (C_4H_8)$, *melting at 69° and boiling at 265°*, is also derived from ar-tetrahydro-α-naphthylamine by means of the diazo-derivative.

ac-**Tetrahydro-β-naphthol**, $C_6H_4 : (C_4H_7OH)$, is an oil, boiling at 264°. It exhibits the character of a fatty alcohol and resembles similarly constituted camphor alcohols, like menthol and borneol (pp. 313, 324).

A series of tetrahydronaphthalene derivatives has been obtained, starting with dihydronaphthalene: Thus, phenol and the latter form **Tetrahydronaphthylphenol**, $C_6H_4 : (C_4H_7 . C_6H_4OH)$ *boiling at 130° (B. 24, 179), while bromine changes it to* **dihydronaphthalene dibromide**, $C_6H_4 : (C_4H_6Br_2)$. Boiling potassium carbonate converts the latter into **Tetrahydronaphthylene Glycol**, $C_6H_4 < \begin{matrix} CH_2-CHOH \\ CH_2-CHOH \end{matrix}$, melting at 135°, which by oxidation is broken down into o-phenylene diacetic acid. It is an analogue of ethylene glycol. The *chlorhydrin* (above), $C_{10}H_{10}Cl(OH)$, melting at 117°, with caustic potash yields **Tetrahydronaphthylene Oxide**, $C_{10}H_{10}O$, melting at 43° and boiling at 258°, *which manifests all the chemical properties of ethylene oxide* (1, 298). Bases have converted the chlorhydrin into a series of "*alkines*," of which mention may be made of—

Trimethyl-oxytetrahydronaphthylene Ammonium Hydroxide,

$C_6H_4 < \begin{matrix} CH_2 . CHOH \\ CH_2 . CHN(CH_3)_3OH \end{matrix}$, because of its intimate connection with choline (1, 309).

The feebler alkalies convert this oxide into the isomeric **β-ketotetrahydronaphthalene**, $C_6H_4 < \begin{matrix} CH_2-CH_2 \\ CH_2-CO \end{matrix}$, melting at 18° and boiling at 138° (16 mm.), which can also be

prepared by the distillation of o-phenylene propionacetic acid (p. 394) (B. **28**, 745). It behaves like a fatty ketone (B. **27**, 1547) with sodium bisulphite, phenylhydrazine, and hydroxylamine. The chlorine addition products of the naphthoquinones are *diketotetrahydronaphthalene derivatives*. They readily part with hydrogen chloride and thus yield substituted naphthoquinones (pp. 404, 405). **Diketotetrahydronaphthylene Oxide,** $C_6H_4<{CO-CH \atop CO-CH}>O$, melting at 136°, is produced by the action of bleaching lime upon α-naphthoquinone (p. 404 and A. **286**, 71).

ac-*Tetrahydronaphthoic Acids* are also classified into aromatic and alicyclic. ar-**Tetrahydro-α-naphthoic Acid,** $COOH.C_6H_3:(C_4H_8)$, with an *amide* melting at 182°, is derived from its nitrile, a rearrangement product from ar-tetrahydro-α-naphthalene diazochloride and potassio-copper cyanide.

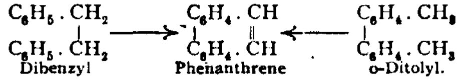
ac-**Tetrahydronaphthoic Acids,** the α- melting at 85° and the β- at 96°, are formed when naphthoic and dihydronaphthoic acids are reduced with sodium amalgam. They resist the action of potassium permanganate more strongly than the dihydro-acids. In comparison with the latter they thus prove themselves to be saturated acids. The long-continued action of the oxidant finally changes them to phthalic and oxalic acids (A. **266**, 202).

ac-**Tetrahydronaphthalene Dicarboxylic Acid,** $C_6H_4[C_4H_6(CO_2H)_2]$, melts at 199°, with the production of its anhydride, melting at 184°. The latter is also formed on heating potassium tetrahydronaphthalene tetracarboxylate, the ester of which has been synthesized from o-xylylene bromide and the sodium derivative of the dimalonic acid ester (p. 391) (B. **17**, 448). **Tetrahydro-1,5-naphthalene Dicarboxylic Acid** melts at 238° (B. **29**, R. 517).

C. **Hexa-, Octo-, Deca-, and Dodeca-hydronaphthalenes,** $C_{10}H_{14}$, $C_{10}H_{16}$, $C_{10}H_{18}$, and $C_{10}H_{20}$, boil at 200°, 185–190°, 173–180°, and 153–158° respectively. They have been obtained by the action of hydriodic acid and phosphorus upon naphthalene (B. **16**, 796, 3032; A. **187**, 164).

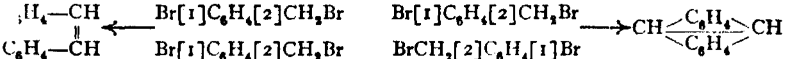
3. PHENANTHRENE GROUP.

Phenanthrene occurs, together with anthracene, in coal-tar and in the so-called "stubb," a mass of substance obtained (together with fluoranthene and pyrene) in the distillation of mercury ores in Idria. It is prepared synthetically (1) (with diphenyl, anthracene, and other hydrocarbons) from various benzene compounds, by conducting their vapors through a red-hot tube—*e. g.*, from toluene, stilbene, diphenyl, and ethylene, and particularly from dibenzyl and o-ditolyl:



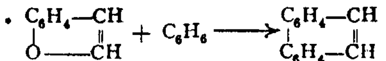
Dibenzyl Phenanthrene o-Ditolyl.

(2) Sodium acting on o-brombenzylbromide also produces it (together with anthracene, p. 421):



Phenanthrene Anthracene.

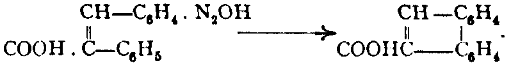
(3) It also appears in the condensation of coumarone with benzene (B. **23**, 85):



Coumarone Phenanthrene.

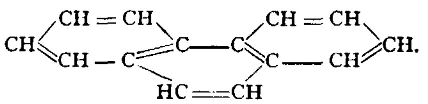
Chrysene is similarly formed from coumarone and naphthalene, and amidonaphthalene (p. 391) from furfurane and aniline.

4. When the diazo-derivative of o-amido-α-phenylacetic acid is acted upon with copper powder phenanthrene carboxylic acids (B. **29**, 496) result:

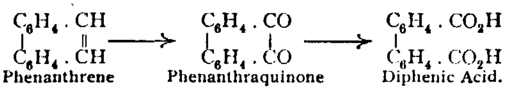


This reaction recalls the formation of diphenyl from benzene and diazobenzene, as well as that of diphenylketone from the diazo-derivative of o-amidobenzophenone (p. 347).

Phenanthrene in accordance with these methods of production must be viewed as a derivative of diphenyl, in which two ortho-positions of the two benzene rings are joined by the group CH = CH, which therefore constitutes, with the four carbon atoms of the two benzene rings, a third normal benzene ring:



The oxidation of phenanthrene leads to a similar conclusion. Phenanthraquinone is the first product, and by continued oxidation it yields diphenic acid or diphenyl-o_2-dicarboxylic acid (p. 340):



Phenanthrene Phenanthraquinone Diphenic Acid.

Phenanthrene, $C_{14}H_{10}$, crystallizes in colorless plates, melting at 99°, and boiling at 340°. It dissolves readily in ether and benzene; but with more difficulty in alcohol and water. The solutions exhibit a blue fluorescence.

The *picric acid* compound, $C_{14}H_{10} . C_6H_2(NO_2)_3 . OH$, separates in yellow needles, melting at 144°. Consult A. **196**, 34; B. **19**, 761, for a method of isolating phenanthrene from crude anthracene.

Hydrogen addition products result upon heating phenanthrene with hydriodic acid and phosphorus. The *Tetra-hydride*, $C_{14}H_{14}$, boils at 314°. The *Per-hydride*, $C_{14}H_{24}$, boils at 270–275° (B. **22**, 779). Chlorine produces substitution products, of which the *octo-chloride*, $C_{14}H_2Cl_8$, melts at 270–280°, and by further chlorination is split into hexachlorbenzene, C_6Cl_6, and CCl_4. Bromine combines with phenanthrene in CS_2 solution, yielding the *dibromide*, $C_{14}H_{10} . Br_2$, which breaks up into hydrogen bromide and *bromphenanthrene*, $C_{14}H_9Br$. This melts at 63°, and is oxidized to phenanthraquinone by chromic acid.

Nitric acid converts phenanthrene into three **nitrophenanthrenes**, which yield three **amido-phenanthrenes**, $C_{14}H_9(NH_2)$, by reduction.

Two *phenanthrene-sulphonic acids* are produced on digesting phenanthrene with sulphuric acid. If these be distilled with yellow prussiate of potash we obtain two *cyanides*, yielding the corresponding carboxylic acids: **α-Phenanthrene Carboxylic Acid**, $CO_2H . C_6H_3 . CH : CH . C_6H_4$, which melts at 266°, and is oxidized to phenanthraquinone carboxylic acid, while the *β-acid*, $C_6H_4 . CH : C(CO_2H)—C_6H_4$, melting at 251°, yields phenanthraquinone. See above for the synthesis of this acid.

Phenanthraquinone, $(C_6H_4)_2(CO)_2$, is formed in the action of chromic acid upon phenanthrene in glacial acetic acid solution; most readily by heating it with a chromic acid mixture (A. **196**, 38). It crystallizes in long, orange-yellow needles, melts at 198°, and distils without decomposition. It dissolves readily in hot alcohol, ether, and benzene, but sparingly in water. It dissolves in concentrated sulphuric acid with a dark green color, and is reprecipitated by water. By adding toluene containing thiotolene and sulphuric acid to the acetic acid solution of phenanthraquinone a bluish-green coloration is produced (see thiophene).

In deportment it recalls β-naphthoquinone. It is odorless, not volatile in steam, unites with one and two molecules of hydroxylamine, and is not reduced by sulphurous acid.

Phenanthraquinone-monoxime, $C_{14}H_8O(N.OH)$, consists of golden yellow needles, melting at 158°. If it is heated together with glacial acetic acid and hydrochloric acid to 130° it sustains the transposition of ketoximes (p. 341), and forms **diphenimide** (B. **21**, 2356):

$$\begin{array}{l} C_6H_4—C:NOH \\ \;| \qquad\quad | \\ C_6H_4—CO \end{array} \longrightarrow \begin{array}{l} C_6H_4—CO \\ \;| \\ C_6H_4—CO \end{array}\!\!\!>NH.$$

The **dioxime** forms an anhydride, $C_{14}H_8\!<\!\begin{array}{c} N \\ \\ N \end{array}\!\!>\!O$, melting at 181°. This is a furazane derivative.

Phenanthraquinone, being an o-diketone, forms phenazine derivatives with o-diamines. See B. **24**, R. 630, 631, for the condensations of acetoacetic ester and acetone. By oxidation with chromic acid, or by boiling with alcoholic potash, phenanthraquinone is oxidized to diphenic acid; ignition with soda-lime produces *diphenylene ketone* (p. 419), *fluorene* (p. 417), and diphenyl. *Diphenylene glycollic acid* (p. 419), *fluorene alcohol*, and *diphenylene ketone* are obtained on boiling with aqueous soda lye. Ignited with zinc-dust we obtain phenanthrene.

When phenanthraquinone is digested with concentrated sulphurous acid it is reduced to **Phenanthrene-hydroquinone**, *Dioxyphenanthrene*, $\begin{array}{l} C_6H_4—C(OH) \\ \;| \qquad\quad \| \\ C_6H_4—C(OH) \end{array}$. This can also be obtained by the reduction of the chloride of diphenic acid (p. 341). With hydriodic acid phenanthraquinone forms **Phenanthrone**, $\begin{array}{l} C_6H_4—CH_2 \\ \;| \qquad\quad | \\ C_6H_4—CO \end{array}$, and with hydriodic acid and phosphorus in glacial acetic acid solution it yields—

Monacetyl-dioxyphenanthrene, $(C_6H_4)_2\!<\!\begin{array}{l} COOC_2H_3 \\ \| \\ COH \end{array}$, which on heating condenses to **Tetraphenylene Furfurane**, $\begin{array}{l} C_6H_4—CH——CH—C_6H_4 \\ \;| \qquad\quad \| \qquad\quad\; \| \qquad | \\ C_6H_4—CH—O—CH—C_6H_4 \end{array}$ (B. **26**, R. 585). When a mixture of phenanthraquinone and aldehydes is exposed to sunlight a union follows with the production of monacidylphenanthrene hydroquinones (A. **249**, 137) (compare **1**, 75).

Retene or **Methyl Isopropylphenanthrene**, $(CH_3)(C_3H_7)C_6H_2\!<\!\begin{array}{c} \text{———} \\ CH:CH \end{array}\!\!>\!C_6H_4$, melting at 98° and boiling at 394°, is a homologue of phenanthrene.

Retene occurs in the tar of highly resinous pines, and in some mineral resins. It is isolated from those portions that boil at elevated temperatures. Its *picric acid compound* forms orange-yellow needles, melting at 123°. Chromic acid in glacial acetic acid solu-

tion oxidizes retene to **retene quinone**, $C_{18}H_{16}O_2$ (*methyl isopropyl phenanthraquinone*), melting at 197°. It resembles phenanthraquinone in its entire deportment. Sodium hydrate converts retene quinone into—

Retene Diphenic Acid, $C_{16}H_{16}<\begin{matrix}CO_2H\\CO_2H\end{matrix}$, and **Retene Glycollic Acid**, $C_{16}H_{16}.C(OH).CO_2H$. Potassium permanganate oxidizes retene quinone to *diphenylene ketone dicarboxylic acid* (p. 419) and **retene ketone**, $CH_3.(C_3H_7).\begin{matrix}C_6H_2\\ |\\ C_6H_4\end{matrix}>CO$ (B. **18**, 1027, 1754, R. 558).

Retene Dodecahydride, *dehydrofichtelite*, $C_{18}H_{30}$, is an oil, boiling at 336°. It is formed when retene is heated with hydriodic acid and phosphorus to 250°, and also in the action of iodine upon **fichtelite**, $C_{18}H_{32}$, melting at 46°, which occurs, together with retene, in the peat of fossil plants (B. **22**, 498, 635, 780, 3369).

Chrysene and **picene** possess a structure similar to that of phenanthrene. They can be derived from phenylnaphthalene and dinaphthyl the same as phenanthrene from diphenyl:

$$\begin{matrix}C_6H_4-CH\\ |\qquad \| \\ C_6H_4-CH\end{matrix}\qquad \begin{matrix}C_6H_4-CH\\ |\qquad \| \\ C_{10}H_6-CH\end{matrix}\qquad \begin{matrix}C_{10}H_6-CH\\ |\qquad \| \\ C_{10}H_6-CH\end{matrix}$$

Phenanthrene Chrysene Picene.

The constitution of these bodies is deduced mainly from the products of their oxidation. Chromic acid first changes them to chrysoquinone and picenoquinone, which can be further transposed into chrysene and picene ketones, chrysenic acid and picenic acid, β-phenylnaphthalene and β-dinaphthyl:

$\begin{matrix}C_6H_4 . CO\\ \vert\qquad \vert \\ C_{10}H_6-CO\end{matrix}$	$\begin{matrix}C_6H_4\\ \vert\\ C_{10}H_6\end{matrix}>CO$	$\begin{matrix}C_6H_5\\ \vert\\ C_{10}H_6.COOH\end{matrix}$	$\begin{matrix}C_6H_5\\ \vert\\ C_{10}H_7\end{matrix}$
Chrysoquinone	Chrysene Ketone	Chrysenic Acid	β-Phenylnaphthalene
$\begin{matrix}C_{10}H_6-CO\\ \vert\qquad \vert \\ C_{10}H_6-CO\end{matrix}$	$\begin{matrix}C_{10}H_6\\ \vert\\ C_{10}H_6\end{matrix}>CO$	$\begin{matrix}C_{10}H_7\\ \vert\\ C_{10}H_6.COOH\end{matrix}$	$\begin{matrix}C_{10}H_7\\ \vert\\ C_{10}H_7\end{matrix}$
Picenoquinone	Picene Ketone	Picenic Acid	β-Dinaphthyl.

Chrysene, $C_{18}H_{12}$, m. p. 250° and b. p. 448°, consists, in a pure condition, of silver-white leaflets with a violet fluorescence. When impure it has a yellow color (hence the name from χρύσεος, gold-yellow). It occurs in those portions of coal-tar which have high boiling points. It can be synthesized from phenyl-naphthyl-ethane, $C_6H_5.CH_2.CH_2.C_{10}H_7$, just as phenanthrene is produced from dibenzyl (p. 413); also by heating naphthalene with coumarone. It is formed in large quantities by heating indene (p. 384); $2C_9H_8 = C_{18}H_{12} + 4H$ (B. **26**, 1544). See B. **24**, 949, for substituted chrysenes. The *hydrides*, $C_{18}H_{28}$, b. p. 360°, and $C_{18}H_{30}$, m. p. 115° and b. p. 353° (B. **22**, 135), result upon heating chrysene with hydriodic acid and phosphorus.

When digested with chromic acid and glacial acetic acid chrysene oxidizes to so-called **Chrysoquinone**, $C_{18}H_{10}O_2$ (a diketone), which crystallizes in red needles, melting at 235°.

Chrysoketone, $C_{17}H_{10}O$, results when chrysoquinone is distilled with lead oxide. Hydriodic acid and phosphorus reduce it to chrysofluorene, $C_{17}H_{12}$.

Chrysenic Acid, $C_{17}H_{12}O_2$ (β-phenylnaphthyl carboxylic acid), is produced when chrysene is fused with caustic alkali. When this acid loses CO_2 it becomes β-phenylnaphthalene (B. **26**, 1745).

Picene, $C_{22}H_{14}$, is the hydrocarbon with the highest melting point (364°). It is formed by the distillation of lignite, coal-tar, and petroleum residues. It can be synthesized from naphthalene and ethylene bromide by means of Al_2Cl_6 (B. **24**, R. 963). It is very sparingly soluble in most of the solvents, but most readily in crude cymene. When heated to 250° with hydriodic acid and phosphorus, **Picene Perhydride**, $C_{22}H_{36}$,

is produced. It melts at 175°. Picene is oxidized by chromic acid to an orange-red *quinone*, $C_{22}H_{12}O_2$, which, like chrysene, is changed on the one hand to *picene ketone*, *picene fluorene alcohol*, and picene fluorene, $(C_{10}H_6)_2CH_2$, and on the other to *picenic acid* or *dinaphthyl-carboxylic acid* and β-dinaphthyl (B. 26, 1751).

4. FLUORENE GROUP.

Just as phenanthrene, chrysene, and picene were regarded as symmetrical o_2-ethylene derivatives of diphenyl, phenylnaphthyl, and dinaphthyl, so *fluorene*, *chrysene-fluorene*, and *picene-fluorene* may be viewed as o_2-methylene derivatives of the last-mentioned hydrocarbons, and accordingly may be designated *diphenylene methane*, *phenylene naphthylene*, and *dinaphthylene-methanes*. Fluorene is also closely allied to diphenylene oxide, diphenylene sulphide, and diphenylene-imide or carbazole (see this), dibenzo-derivatives of furfurane, thiophene, and pyrrol:

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CH_2 \qquad \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!O \qquad \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!S \qquad \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!NH$$

Fluorene — Diphenylene Oxide — Diphenylene Sulphide — Diphenylene-imide.

General Methods of Formation:

1. Fluorene is formed by conducting vapors of diphenylmethane through tubes heated to redness; chrysofluorene is similarly obtained from β-naphthyl phenylmethane:

$$(C_6H_5)_2CH_2 \longrightarrow (C_6H_4)_2CH_2.$$

2. o-Diphenyl carboxylic acid, phenylnaphthyl carboxylic acid or chrysenic acid, and dinaphthyl carboxylic or picenic acid, when heated alone or in the form of salts, yield fluorene, chrysene, and picene ketones, which can be readily reduced to fluorene, chrysofluorene, and picene-fluorene; conversely, the acids are reformed when the ketones are fused with caustic potash:

$$\begin{matrix} C_6H_4\,.\,COOH \\ | \\ C_6H_5 \end{matrix} \quad \begin{matrix} \longrightarrow \\ \longleftarrow \end{matrix} \quad \begin{matrix} C_6H_4 \\ \\ C_6H_4 \end{matrix}\!\!>\!CO.$$

3. Fluorene ketone is also obtained from the diazo-derivative of o-amidobenzophenone by the elimination of nitrogen; similarly, chrysene ketone is formed from o-amidophenyl-α-naphthyl-ketone (B. 29, 826):

$$C_6H_4{<}^{N_2OH}_{CO}{>}C_6H_5 \longrightarrow C_6H_4{<}^{____}_{CO}{>}C_6H_4.$$

4. Phenanthraquinone, chrysoquinone, and picenoquinone, when oxidized, also yield the ketones of the corresponding fluorenes:

$$\begin{matrix} C_6H_4-CO \\ | \qquad\ \ | \\ C_6H_4-CO \end{matrix} \longrightarrow \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CO.$$

Fluorene, *Diphenylene Methane*, $C_{13}H_{10}$, m. p. 113° and b. p. 295°, crystallizes in colorless leaflets with a violet fluorescence. It forms a compound with picric acid, melting at 81°. It results upon exposing diphenyl methane to a high heat (above), and in the reduction of diphenylene ketone with zinc dust or upon heating it to 160° with HI and phosphorus. The chromic acid mixture oxidizes it to diphenylene ketone.

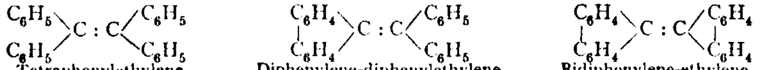
Methylhexahydrofluorene, boiling at 128° (14 mm.), results from the action of P_2O_5 upon methylbenzylcyclohexanol, the reduction product of benzylidene-methyl-cyclohexanon, $(CH_3)(OH)C_6H_9:CH_2.C_6H_5 \longrightarrow (CH_3)C_6H_9.CH_2.C_6H_4$ (B. **29**, 2962), produced in the condensation of benzaldehyde and methyl-cyclo-hexanon.

Retene-fluorene, *methylisopropyldiphenylenemethane*, $\begin{matrix}(CH_3)(C_3H_7)C_6H_2\\ |\\ C_6H_4\end{matrix}\!\!>CH_2$, melting at 92°, is derived from its ketone upon distillation with zinc-dust. **Chrysofluorene**, *naphthylene-phenylene-methane*, $C_{10}H_6—CH_2—C_6H_4$, melting at 180°, is derived from β-benzylnaphthalene or from chryso-ketone. An isomeric **isochryso-fluorene**, melting at 76°, is obtained from α-benzylnaphthalene (B. **27**, 953). **Picene-fluorene**, *phylen-methane*, $(C_{10}H_6)_2CH_2$, melting at 306°, is produced on heating its ketone to 160–175° with hydriodic acid (A. **284**, 70).

Diphenylene-phenylmethane, ms.-*Phenyl-fluorene*, $(C_6H_4)_2CHC_6H_5$, melting at 146°, results on heating triphenylmethane chloride, $(C_6H_5)_3CCl$, or potassium triphenylmethane (p. 351); from fluorene alcohol, benzene, and sulphuric acid (B. **22**, R. 660), and by distilling hydrofluoranic acid (p. 362) over soda-lime.

Diphenylene-diphenyl-ethane, $(C_6H_4)_2CH.CH(C_6H_5)_2$, melting at 217°, and **Diphenylene-diphenyl-ethylene**, $(C_6H_4)_2C:C(C_6H_5)_2$, melting at 229°, arise in the breaking-down of *diphenylene-diphenyl-succinic anhydride*, $\begin{matrix}(C_6H_4)_2.C.CO\\ |\\ (C_6H_5)_2.C.CO\end{matrix}\!\!>O$, melting at 256°, one of the reaction-products of cold concentrated sulphuric acid upon benzilic acid (p. 369). Diphenylene-diphenyl-ethylene is produced on heating benzophenone chloride with fluorene. It consists of *colorless* crystals, the solutions of which are *colored intensely yellow*. The moderated oxidation of this body with chromic acid gives rise to **diphenylene-diphenyl-pinacoline**, melting at 172°. Its structure is unsymmetrical: $(C_6H_4)_2C(C_6H_5)CO.C_6H_5$, because it is decomposed by alcoholic caustic potash into diphenylene phenylmethane and benzoic acid. It also results from potassium triphenylmethane and benzoylchloride (B. **29**, 2152).

Bidiphenylene Ethane, $(C_6H_4)_2CH.CH(C_6H_4)_2$, colorless needles, melting at 246°, is produced, together with **bi-diphenylene Ethylene**, *bifluorene*, $(C_6H_4)_2C:C(C_6H_4)_2$, melting at 188°, on heating fluorene with lead oxide. The second hydrocarbon is also formed on heating fluorene with bromine, chlorine, or sulphur. It consists of beautiful *red*-colored needles. Its bromine addition product is colorless, and when heated with sodium in xylene solution it reverts to the red hydrocarbon (B. **25**, 3140; A. **290**, 238; **291**, 1). The following diagram is interesting from the point of view of the color of highly condensed hydrocarbons:



Tetraphenylethylene (p. 378). Colorless | Diphenylene-diphenylethylene. Colorless; yellow in solution | Bidiphenylene-ethylene. Red needles.

Compare the yellow color of acenaphthylene (p. 410). Chromic acid oxidizes bi-diphenylene-ethylene into a **pinacoline**, melting at 258° (together with fluorenone), which probably, like diphenylene-diphenyl pinacoline, possesses an unsymmetrical structure corresponding to the formula $\begin{matrix}(C_6H_4)_2:C—C_6H_4\\ |\quad\quad |\\ OC—C_6H_4\end{matrix}$, because, like the diphenylene-diphenyl pinacoline, it is resolved by alcoholic potash into the acid $(C_6H_4):CH—C_6H_4.C_6H_5.COOH$. The pinacoline is also produced in the reduction of fluorenone with zinc-dust and acetyl chloride. It is further identical with the bidiphenylene-ethine oxide (B. **29**, 2152; A. **291**, 1), produced on heating bidiphenylene-ethine dibromide with water.

Fluorene Alcohol, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CH.OH$, melting at 153°, results in the action of sodium amalgam upon diphenylene ketone and by heating sodium diphenylene glycollic acid to 120°. Concentrated sulphuric acid or P_2O_5 colors it an intense blue, and produces *fluorene ether*, $(C_{13}H_9)_2O$, melting at 290°.

Retene-, chrysene-, and picene-fluorene alcohols, melting at 134°, 167°, and 230° respectively, are obtained by methods similar to those pursued in the preparation of fluorene alcohol.

Diphenylene Ketone, Fluorenone, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>CO$, *melting at 84° and boiling at 341°* (B. **27**, R. 641), is obtained from diphenic acid, isodiphenic acid, and o-diphenyl carboxylic acid when heated with lime; by oxidizing fluorene with a chromic acid mixture, and by heating phenanthraquinone with caustic lime (A. **196**, 45; **279**, 257), and when the diazo-compound of o-amido-benzophenone (p. 347) is heated with water (B. **28**, 111). Potassium permanganate oxidizes it to phthalic acid. It is converted into o-phenyl benzoic acid on fusion with potassium hydroxide. Its *oxime*, $(C_6H_4)_2C : NOH$, melts at 193° (see p. 420); the *phenylhydrazone* melts at 151° (B. **29**, 230, R. 26).

Retene Ketone, $(C_3H_7)(CH_3)C_6H_2 . CO . C_6H_4$, melts at 90°. **Chrysoketone,** $C_6H_4 . CO . C_{10}H_6$, melts at 130°. See p. 418 for the production from o-amidophenyl-α-naphthyl ketone. **Picene Ketone,** $(C_{10}H_6)_2CO$, melts at 185°.

o-**Oxydiphenylene Ketone,** *Oxyfluorenone*, $C_6H_3(OH) . CO . C_6H_4$, melting at 115°, is obtained from sym. o-diamidobenzophenone (p. 347) on boiling its diazo-salts with water. It forms yellow-red or dark-red alkali salts, which manifest a feeble dye nature. When fused with caustic potash it decomposes into o-phenylsalicylic acid, $C_6H_5 . C_6H_3(OH)COOH$, which is recondensed by concentrated sulphuric acid to oxydiphenylene ketone (B. **23**, 112). o-Oxydiphenylene ketone is also prepared from o-**amido-diphenylene ketone**, melting at 138°, which is obtained from diphenylene ketone carboxylamide (p. 420) with bromine and caustic potash (Hofmann's amine reaction). When o-amido-diphenylene ketone is fused with caustic potash it is rearranged into phenanthridone (B. **28**, R. 455):

$$C_6H_3(NH_2)-CO-C_6H_4 \longrightarrow C_6H_3-NH-CO-C_6H_4,$$

which also results by Beckmann's transposition on heating the oxime of fluorenone with zinc chloride (B. **29**, 230):

$$C_6H_4-C:(NOH)-C_6H_4 \longrightarrow C_6H_4-NH . CO-C_6H_4.$$

Carboxylic Acids: **Diphenylene Acetic Acid,** *Fluorene Carboxylic Acid*, $(C_6H_4)_2CH . CO_2H$, melting at 221°, results on reducing diphenylene glycollic acid with hydriodic acid and phosphorus.

Diphenylene Glycollic Acid, ms-Oxyfluorene Carboxylic Acid, $(C_6H_4)_2C(OH) . CO_2H$, melting at 162°, is produced when phenanthraquinone is boiled with sodium hydroxide. In this instance an atomic rearrangement occurs, similar to that observed in the transition of benzil to benzilic acid, or of β-naphthoquinone to oxyindene carboxylic acids (p. 386):

$$\begin{matrix} C_6H_5CO \\ | \\ C_6H_5CO \end{matrix} \xrightarrow{H_2O} \begin{matrix} C_6H_5 \\ \\ C_6H_5 \end{matrix}\!\!>C(OH) . COOH \qquad \begin{matrix} C_6H_4-CO \\ | \quad\;\; | \\ C_6H_4-CO \end{matrix} \xrightarrow{H_2O} \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>C(OH)COOH.$$

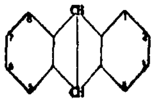
It is decomposed by concentrated sulphuric acid or upon heating, when carbon dioxide and water split off and *fluorene ether* results. Chromic acid oxidizes it to diphenylene ketone. Analogues of diphenylene glycollic acid have been obtained from retene- and chrysene-quinone (above).

Diphenylene-ketone Carboxylic Acids, $C_6H_4 . CO . C_6H_3 . CO_2H$. The *α-acid*, melting at 191°, is produced by the oxidation of fluoranthene with a chromic acid mixture. Sodium amalgam converts it into *α-fluorenic acid*, $C_6H_4 . CH_2 . C_6H_3 . CO_2H$,

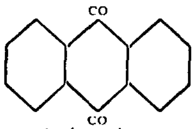
The methods just given and a series of others—*e. g.*, the production of anthraquinone from o-tolylphenyl ketone and lead oxide, and that of anthracene and methyl anthracene from o-tolylphenylketone and o-ditolylketone by means of zinc-dust (B. **23**, R. 198)—demonstrate the accepted symmetry of the derivatives of anthracene, which is further proved by the following fact: brominated o-benzoylbenzoic acid from o-phthalic acid (p. 350) yields bromanthraquinone; the oxyanthraquinone obtained from the latter, however, can be oxidized to o-phthalic acid; so that both in the synthesis and decomposition of the molecule o-phthalic acid appears, which, in the first instance, is connected with the one and in the second case with the second half of the molecule (compare constitution of naphthalene, p. 389) (B. **12**, 2124):

$$Br.C_6H_3\left\{\begin{matrix}[1]CO.C_6H_5\\ [2]COOH\end{matrix}\right. \longrightarrow OH.C_6H_3\left\{\begin{matrix}[1]CO[1]\\ [2]CO[2]\end{matrix}\right\}C_6H_4 \longrightarrow \left.\begin{matrix}HOOC[1]\\ HOOC[2]\end{matrix}\right\}C_6H_4.$$

Therefore, anthraquinone and anthracene, genetically connected with it, have a symmetrical constitution corresponding to the symbols:



Anthracene



Anthraquinone.

Anthracene is a nucleus resulting from the condensation of three benzene nuclei, of which the intermediate or middle member shows a para-union. The positions 1, 4, 5, 8 (α-) are alike; also 2, 3, 6, 7 (β-). By the replacement of the middle hydrogen atoms of anthracene γ-derivatives or *meso*-derivatives are obtained. In contrast with this the substituents of the two outer benzene nuclei are designated by the prefix *benz.* In most of the anthracene transpositions the intermediate C-atoms are first attacked.

Anthracene, $C_{14}H_{10}$, melting at 213° and boiling at 351°, is isomeric with tolane (p. 371) and phenanthrene (p. 413), and is produced according to the methods indicated upon p. 421. (See also B. **28**, R. 148.) It is found in large quantities in coal-tar.

Crude anthracene, boiling at 340–360° and beyond, is best purified by treating it with liquid sulphurous acid, which chiefly takes up the admixtures (B. **26**, R. 634). For additional methods of purification see B. **18**, 3034; **21**, R. 75; A. **191**, 288. Chemically pure anthracene is prepared by heating anthraquinone with zinc-dust.

Anthracene crystallizes in colorless monoclinic tables, showing a beautiful blue fluorescence. It dissolves with difficulty in alcohol and ether, but easily in hot benzene. Picric acid unites with it, yielding $C_{14}H_{10}$.-$C_6H_2(NO_2)_3OH$, crystallizing in red needles, and melting at 138°.

When the cold saturated solution of anthracene in benzene, or, better, in xylene (B. **26**, R. 547), is exposed to sunlight, a dimolecular modification of anthracene, ***Para-anthracene***, $(C_{14}H_{10})_2$, separates out in plates. It dissolves with difficulty in benzene, is not attacked by nitric acid or bromine, melts at 244°, and in so doing reverts to common anthracene.

Alkylic Anthracenes: (a) $C_6H_4\left\langle\begin{matrix}CH\\ |\\ CH\end{matrix}\right\rangle C_6H_3R$; (b) $C_6H_4\left\langle\begin{matrix}CR\\ |\\ CH\end{matrix}\right\rangle C_6H_4$

Benz-alkyl Derivatives — ms- or γ-Alkyl Derivatives.

(a) The benz-mono-alkylic anthracenes can exist in two isomerides (α- and β-).

Methyl Anthracene, $C_6H_4(CH)_2C_6H_3.CH_3$, melting at 190°, occurs in crude anthracene, and resembles anthracene. It is obtained on conducting the vapors of ditolyl-methane and ditolyl-ethane through a red-hot tube; also on heating emodin

and chrysophanic acid (hydroxylmethyl-anthraquinones) with zinc-dust, as well as by prolonged boiling of benzoyl xylene, $C_6H_5 . CO . C_6H_3(CH_3)_2$. Concentrated nitric acid converts it into **Methyl-anthraquinone.** Anthraquinone-carboxylic acid is produced when methyl-anthracene, dissolved in glacial acetic acid, is oxidized by chromic acid.

Benz-**dimethylanthracenes,** $C_{14}H_8(CH_3)_2$, melting at 200° and 225°, are obtained from xylyl chloride, and from toluene and CH_2Cl_2 by means of Al_2Cl_6, according to methods 2 and 3 (p. 421). A dimethyl anthracene has been isolated from the high-boiling aniline oils.

(b) Meso- or γ-Alkyl Anthracenes are obtained from the alkylic hydranthranols, $C_6H_4<\frac{CR(OH)}{CH_2}>C_6H_4$, by the elimination of water. This happens on boiling them with alcohol, hydrochloric acid, or picric acid (A. **212,** 100). Alkylic oxanthranols are formed upon oxidation: γ-**ethyl, isobutyl,** and **amyl anthracenes,** melting at 60°, 57°, and 59°. γ-**Phenyl anthracene,** $C_{14}H_9(C_6H_5)$, melting at 152°, is obtained from phenyl anthranol (p. 424) with zinc-dust.

γ-**Dimethyl Anthracene,** $C_6H_4(C . CH_3)_2C_6H_4$, melting at 179°, is derived from its dihydride, the condensation product obtained from ethidene chloride and benzene by means of Al_2Cl_6 (p 424) (see B. **21,** 1176).

Substituted Anthracenes: Chlorine and bromine acting upon the CS_2-solution of anthracene first substitute the middle CH-groups with the production of γ-**mono- and dihalogen anthracenes.** γ-Dibrom-anthracene is also formed by the action of bromine upon anthracene hydride (p. 424).

When anthracene is introduced into concentrated nitric acid, free from NO_2, ms-**Dinitroanthracene,** $C_6H_4(C . NO_2)_2C_6H_4$, results. When this is carefully heated it sublimes without decomposition; if, on the contrary, it be rapidly heated, it decomposes readily into NO and anthraquinone: $C_6H_4(C . NO_2)_2C_6H_4 \longrightarrow 2NO + C_6H_4(CO)_2C_6H_4$. Fuming nitric acid and alcohol convert anthracene into **anthracene ethyl nitrate,** $C_6H_4<\frac{CH(OC_2H_5)}{CH\ (NO_2)}>C_6H_4$, which also quickly changes to anthraquinone, but with alcoholic potash yields *pseudo-nitroso-anthrone*, $C_6H_4<\frac{C(OH)}{C(NO)}>C_6H_4$ (B. **24,** R. 652, 947).

β-**Amido-anthracene,** *Anthramine*, $C_6H_4(CH)_2C_6H_3 . NH_2$, melting at 237°, and meso- or γ-**Amido-anthracene,** decomposing at 115°, are produced on heating β-anthrol and anthranol (see below) with ammonia. meso-**Diamidoanthracene,** C_6H_4-$(C . NH_2)_2C_6H_4$, melting at 146°, results from the reduction of ms-dinitroanthracene.

Anthracene Sulphonic Acids result on treating anthracene with sulphuric acid and in the reduction of anthraquinone sulphonic acids (p. 426). Anthracene carefully treated with dilute sulphuric acid yields—

Anthracene Mono-sulphonic Acid, $C_{14}H_9 . SO_3H$; its *chloride* melts at 122° (B. **28,** 2258). Concentrated sulphuric acid produces—

α- and β-**Anthracene Disulphonic Acids,** which form dioxyanthracenes on fusion with caustic potash.

Oxyanthracenes: (1) $C_6H_4<\frac{CH}{CH}>C_6H_3OH$. (2) $C_6H_4<\frac{COH}{CH}>C_6H_4$.

(1) α- and β-**Monoxy-anthracene,** α- and β-**Anthrol,** behave like phenols or naphthols. β-Anthrol, from β-anthracene sulphonic acid and β-oxyanthraquinone, is changed by nitrous acid to α-**Nitroso**-β-**anthrol,** $C_6H_4(CH)_2C_6H_2(OH)(NO)$, which, upon reduction, yields α-**Amido**-β-**anthrol.** The latter may be oxidized to β-**anthraquinone,** $C_6H_4<\frac{CH - C - CO - CO}{CH - C - CH - CH}$ (?), melting with decomposition at 180°, and isomeric with β-naphthoquinone. It corresponds to β-naphthoquinone (B. **27,** 1438). It is only after the OH-group has been acetylated that the anthrols can be oxidized to oxyanthraquinones (see oxidation of phenols, p. 143).

Benz-**Dioxyanthracenes:** Two isomerides,—**Chrysazol** and **Rufol,**—having the formula $OH . C_6H_3 : (CH)_2 : C_6H_3OH$, are obtained from α- and β-anthracene disul-

When anthraquinone is heated with sulphuric acid, or when anthracene sulphonic acids are oxidized, various **anthraquinone-mono-** and **di-sulphonic acids** are produced. When these are fused with caustic potash, mono- and poly-oxyanthraquinones are formed. Some of these are valuable dyes:

β-Anthraquinone-monosulphonic Acid	→ Oxyanthraquinone → Alizarin (2OH)
α-Anthraquinone-disulphonic Acid	→ Anthraflavic Acid (2OH) → Flavopurpurin (3OH)
β-Anthraquinone-disulphonic Acid	→ Isoanthraflavic Acid (2OH) → Anthrapurpurin (3OH)
γ-Anthraquinone-disulphonic Acid	→ Chrysazine (2OH) → Oxychrysazine (3OH)
δ-Anthraquinone-disulphonic Acid	→ Anthrarufin (2OH) → Oxyanthrarufin (3OH).

The **Oxyanthraquinones** are derived (1) from the brom- and chlor-anthraquinones and from the sulphonic acids on fusion with alkalies, when the substituting groups are replaced by hydroxyls.

By stronger fusion there generally ensues an additional entrance of hydroxyl (oxy- and dioxyanthraquinones result from the mono-sulphonic acids); the same is true in the fusion of the oxyanthraquinones (B. **11**, 1613).

(2) The oxyanthraquinones may be synthetically prepared on heating phthalic anhydride with phenols (mono- and poly-valent) and sulphuric acid to 150°. The m-oxybenzoic acids (p. 421) also yield them when similarly treated.

The introduction of hydroxyl into anthraquinone and the oxyanthraquinones can be effected practically by persulphates in sulphuric acid solution. One or several hydroxyl groups will then enter the anthraquinone molecule, depending upon the conditions which prevail (B. **29**, R. 988).

Continued fusion with alkalies causes the oxyanthraquinones to separate into their component oxybenzoic acids (same as anthraquinone decomposes into benzoic acid), and this reaction aids in the determination of the position of the isomerides (B. **12**, 1293; A. **280**, 1).

All anthraquinones are reduced to anthracene when heated with zinc-dust.

Individual hydroxyls in the oxyanthraquinones are reduced by heating the latter with stannous chloride and sodium hydroxide (A. **183**, 216). Heated to 150–200° with ammonia water, single OH-groups are replaced by amide groups.

(a) *Monoxyanthraquinones*, $C_{14}H_7O_2(OH)$, the α- or **Erythro-oxyanthraquinone**, melting at 190°, and the β- at 323°, are formed simultaneously on heating together phenol and phthalic anhydride. The β-body is also prepared from β-brom- or sulpho-anthraquinone.

Both oxyanthraquinones yield *alizarin* when fused with caustic potash.

(b) *Dioxyanthraquinones:* The members of this group containing two OH-groups in the 1,2-position (p. 422) are especially interesting, because they unite with metallic oxides to form insoluble, very stable ***lakes***, which adhere closely to the fiber. Their color varies with the character of the metal. They are, therefore, very valuable mordant dyes (B. **21**, 435, 1164) (compare the similar behavior of the dioxybenzophenones, p. 348, of ***naphthazarine***, p. 405, etc. For the theoretical side

consult B. **26**, 1574). Alizarin, 1,2-dioxyanthraquinone, is the most important of these dyes.

Nine of the ten possible isomeric dioxyanthraquinones are known.

Alizarin, 1,2 *Dioxyanthraquinone*, melting at 290° and subliming at higher temperatures in orange-red needles, is the chief constituent of the dye of the madder root (*Rubia tinctorium*), in which it is contained as *ruberythric acid* (identical with morindin, from *Morinda citrifolia*).

Through the action of a ferment in the madder root, or when it is boiled with dilute acids or alkalies, ruberythric acid decomposes into glucose and alizarin:

$$\text{Ruberythric acid}\quad C_{26}H_{28}O_{14} + 2H_2O = 2C_6H_{12}O_6 + C_{14}H_6O_2(OH)_2 \quad \text{Alizarin.}$$

The alizarin products (*garancin*, etc.) obtained by such decompositions of madder root were formerly used in dyeing. At present they have been almost entirely supplanted by pure synthetic alizarin.

Artificial alizarin was first obtained by Graebe and Liebermann, in 1868, by heating dibrom-anthraquinone with potassium hydroxide. They had previously observed that the natural alizarin yielded anthracene when it was heated with zinc-dust. Alizarin is also produced from dichlor- and monobrom-anthraquinone, from the two oxyanthraquinones and anthraquinone sulphonic acid, by fusion with caustic potash.

Technically, it is made from anthraquinone prepared from purified (50 per cent.) anthracene. The latter is converted by fuming sulphuric acid into anthraquinone-monosulphonic acid, which is then fused under pressure for several days with caustic soda at a temperature ranging from 180–200°. Potassium chlorate is added as an oxidizing agent. The product of the reaction is sodium-alizarin, which is then decomposed with hydrochloric acid and brought into the market in the form of a paste (10–20 per cent.).

Alizarin also results, together with isomeric hystazarin, on heating phthalic anhydride with pyrocatechin and sulphuric acid.

Alizarin dissolves readily in alcohol and ether, and sparingly in hot water. It dissolves with a purple-red color in the alkalies; lime and barium salts throw out the corresponding salts as *blue* precipitates. Alums and tin salts produce *red-colored* precipitates (madder lakes); while ferric salts form *blackish-violet* and chromium salts *violet-brown* precipitates.

In cotton dyeing and printing the beautiful red lake and the almost black iron lake are generally employed. The goods are mordanted with alumina (by immersing them in aluminium-acetate, then heating, whereby aluminium hydroxide is deposited on the fibers) and then dipped into the solution of alizarin; the resulting alizarin-aluminate is fixed by the fibers. In dyeing with turkey-red it is customary to mordant the cloth with oil and alum, when the alumina then unites both with the oleic acid and with the alizarin.

Alizarin is decomposed by protracted fusion with caustic potash into benzoic and protocatechuic acids.

β-**Nitroalizarin**, *Alizarin Orange*, $C_6H_4(CO)_2C_6H(OH)_2(3)NO_2$, consists of orange-red leaflets, melting at 244°. It is produced by nitrating alizarin in glacial acetic acid or by the action of NO_2-vapors. It is prepared technically. Its alumina lake is *orange* in color. *Alizarin-blue*, a derivative of anthraquinoline (B. **18**, 447), results upon heating it with glycerol and sulphuric acid (see Skraup's quinoline synthesis).

β-**Amido-alizarin** results by the reduction of *β*-nitroalizarin. Acetic anhydride converts it into an ethenyl compound, which proves that the amido-group occupies an ortho position relatively to a hydroxyl group (B. **18**, 1666).

Isomeric **α-nitro-alizarin** (1,2,4) is obtained by the nitration of **diaceto-alizarin**. It melts at 195° (compare B. 24, 1610).

Alizarin-amide, $C_{14}H_6O_2<^{NH_2}_{OH}$, obtained by heating alizarin with ammonia-water to 200°, melts at 225°.

When nitro-anthraquinones are reduced hydroxylamidoanthraquinones are formed; these can be rearranged by sulphuric acid into amido-oxyanthraquinones.

Three of the dioxyanthraquinones isomeric with alizarin contain the OH-groups in one benzene nucleus. They are:

(1,3)-**Purpuroxanthin**, from phthalic anhydride and resorcinol; (1,4)-**quinizarin**, from hydroquinone; and, (2,3)-**hystazarin**, from pyrocatechin (B. 28, 116). They are prepared more advantageously from their *ethers*, which result by the condensation of the corresponding dioxy-benzene ethers with phthalic anhydride and Al_2Cl_6.

The following heteronuclear dioxyanthraquinones are produced when m-oxybenzoic acid is heated:

(1.5)-**Anthrarufin**, (1,7)-**Metadioxyanthraquinone**, (2,6)-**Anthraflavic Acid. Isoanthraflavic Acid** is obtained from β-anthraquinone-sulphonic acid. **Chrysazin** is another isomeride. It is obtained from its tetranitro-compound, $C_{14}H_2(NO_2)_4(O_2)(OH)_2$, the so-called **chrysammic acid**, by reduction and the replacement of the amid-groups. This latter acid is obtained when aloës are digested with concentrated nitric acid. Consult B. 19, 2327, upon the spectra of the dioxyanthraquinones.

Homologous Dioxyanthraquinones: **Dioxymethylanthraquinone**, $C_{14}H_5(CH_3)O_2(OH)_2$, is **chrysophanic** or **Rheïnic Acid**, melting at 178° (A. 284, 193). It exists in senna leaves (of the *Cassia* varieties) and in the root of rhubarb (from the *Rheum* variety). Zinc-dust reduces it to methyl anthracene.

Chrysarobin, $C_{30}H_{26}O_7$, a reduction product of chrysophanic acid, occurs in goa- and arroroba-powder. Air oxidizes its alkaline solution to chrysophanic acid. The same occurs in the animal organism (B. 21, 447).

Methyl-alizarin, melting at 250–252°, is isomeric with dioxymethylanthraquinone. It is obtained from methyl-anthraquinone sulphonic acid. It is very similar to alizarin.

Various **methylpurpuroxanthins** have been prepared by the condensation of 1,3,5-dioxybenzoic acid with o- and m-toluic acids (B. 29, R. 141).

Dimethyl-anthrarufin, $(CH_3)(OH)C_6H_2(CO)_2C_6H_2(CH_3)(OH)$, can also be obtained by the action of sulphuric acid upon sym. oxytoluic acid (B. 22, 3273).

(c) *Trioxyanthraquinones.*

These are produced on oxidizing anthraquinone disulphonic acids and dioxyanthraquinones, or upon fusing them with alkalies.

Purpurin, $C_6H_4<^{CO}_{CO}>C_6H[1,2,4](OH)_3 + H_2O$, melting at 253° (anhydrous) and sublimable, is present with alizarin in the madder root. It is prepared artificially by heating alizarin and quinizarin with manganese dioxide and sulphuric acid to 150°. Is is also obtained from tribromanthraquinone. It dissolves with a pure red color in hot water, alcohol, ether, and the alkalies. Lime and baryta-water yield purple-red precipitates. It yields a beautiful scarlet red with alumina mordants.

Purpurin-amide, $C_{14}H_5O_2(OH)_2NH_2$, is obtained on digesting purpurin with aqueous ammonia at 150°.

The following are isomerides of purpurin: **anthragallol** (1,2,3), a constituent of *alizarin brown*, **anthra-** or **isopurpurin** (1,2,7), and **flavopurpurin** (1,2,6), applied technically in dyeing and printing, and also **oxychrysazin** (1,2,5?). Consult A. 280, 1, for the determination of the constitution of these bodies from the decompositions of the disulphonic acids genetically connected with them.

Homologous Trioxyanthraquinones: **Emodin**, and a **trioxymethylanthraquinone**, melting at 203° and isomeric with it, are formed, together with rhamnose, by the decomposition of *frangulin*, from the bark of *Rhamnus frangula*, by means of alcoholic

hydrochloric acid (B. **25**, R. 371). Emodin also results from the decomposition of *polygonine*.

(d) *Tetra- and Poly-oxyanthraquinones*: When oxyanthraquinones are heated with fuming sulphuric acid, new hydroxyls enter these bodies, para-hydrogen atoms of the non-substituted nucleus being replaced (J. pr. Ch. [2], **43**, 231; **44**, 103). Thus, alizarin yields **quinalizarin**, *alizarin-bordeaux*, $C_{14}H_4O_2$-1,2,5,8-$(OH)_4$.

Two tetraoxyanthraquinones, **anthrachrysone** and **rufiopin**, are obtained by heating symmetrical dioxybenzoic acid and opianic acid (p. 237) or protocatechuic acid (p. 227) with sulphuric acid.

Rufigallic Acid is a hexa-oxy-anthraquinone, $C_{14}H_2O_2$ - 1,2,3,5,6,7 - $(OH)_6$, which is formed when gallic acid is heated with sulphuric acid. It dissolves with an indigo-blue color in alkalies.

It dyes chrom-mordanted material brown. It appears in trade in conjunction with anthrapurpurin as *alizarin* or *anthracene brown*. *Anthracene blue*, formed by the action of fuming sulphuric acid upon dinitroanthraquinone, is an isomeric hexaoxyanthraquinone.

Anthraquinone Carboxylic Acids: α- and β-**Anthraquinone Carboxylic Acids** are produced in the oxidation of anthracene carboxylic acids. The α-acid (m. p. 285°) is also formed in the condensation of benzoyl phthalic acid and isophthalic acid (B. **29**, R. 284), and the β-acid when chromic acid acts upon methylanthracene. The amide of the α-acid, treated with bromine and alkali, yields 1-amidoanthraquinone (p. 425; B. **30**, 1115). **Trioxyanthraquinone Carboxylic Acid**, *purpurin carboxylic acid*, $C_{14}H_4\cdot O_2(OH)_3CO_2H$, is **pseudo-purpurin**, which occurs in crude purpurin (from madder). On heating, it decomposes into carbon dioxide and purpurin.

See C. 1894, II, 784, for the synthetic purpurin carboxylic acids.

Naphanthracene, $C_6H_4\left<\begin{matrix}CH\\|\\CH\end{matrix}\right>C_{10}H_6$, melting at 141°, may be included among the homologous anthracenes. It is isomeric with chrysene (p. 416). It is formed when its quinone is digested with zinc-dust and ammonia.

Naphanthraquinone, $C_6H_4(CO)_2C_{10}H_6$, melting at 168°, is obtained from naphtoyl-o-benzoic acid, $C_6H_4\left<\begin{matrix}COOH\\CO\,.\,C_{10}H_7\end{matrix}\right.$, the same as anthraquinone from benzoyl-benzoic acid (B. **19**, 2209; **29**, 827).

GLYCOSIDES OR GLUCOSIDES AND PENTOSIDES.

Glycosides or glucosides are those vegetable substances which break down into sugars, chiefly grape sugar or glucose, and other bodies, when they are exposed to the action of unorganized ferments, enzymes (1, 587). Some of them decompose into isodulcite or rhamnose, a pentose, hence they are designated as *pentosides*. In many glycosides the exact nature of the sugar is not known. The glycosides and pentosides are therefore to be regarded as ethereal sugar derivatives. Some of them were described under their decomposition products, while many have been synthesized.

E. Fischer demonstrated that the simplest glucosides could be prepared by the action of hydrochloric acid upon alcoholic sugar solutions; they have been described (1, 549).

1. **Myronic Acid**, $C_{10}H_{19}NS_2O_{10}$, occurs as potassium salt in the seeds of black mustard. This crystallizes from water in bright needles. On boiling it with baryta-water, or by the action of the ferment *myrosin*, present in the seed, the salt decomposes into *glucose*, *allyl mustard oil*, and primary potassium sulphate.

2. **Arbutin**, $C_{12}H_{16}O_7$, and **Methyl Arbutin**, $C_{13}H_{18}O_7$, are found in the leaves of *Arbutus uva ursi*. Arbutin crystallizes in fine needles, with ½-1 molecule of water,

and melts at 187° (B. **16**, 800) in the anhydrous state. *Methyl Arbutin* melts at 176°. It is formed artificially from arbutin by the action of methyl iodide and potash.

By their decomposition we get, besides grape sugar, hydroquinone or methyl hydroquinone:

$$C_{12}H_{16}O_7 + H_2O = C_6H_{12}O_6 + C_6H_4(OH)_2.$$

3. **Salicin,** $C_{13}H_{18}O_7$, *saligenin, glucose,* melting at 188°, occurs in the bark and leaves of willows—*e. g.*, *Salix helix*—and some poplars, from which it may be extracted with water. It can be artificially prepared by reducing helicin with sodium amalgam. It forms shining crystals, which dissolve easily in hot water and alcohol, and melt at 198°. Its taste is bitter.

Oxidants convert it into ***helicin,*** hence the saligenin in salicin is linked by means of the phenol oxygen atom with the glucose. The enzymes *ptyalin* and *emulsin* (1, 587) decompose salicin into glucose and saligenin (p. 217):

$$C_6H_{11}O_5 . O . C_6H_4 . CH_2 . OH + H_2O = C_6H_{12}O_6 + HO . C_6H_4 . CH_2 . OH.$$

Boiling dilute acids decompose it in a similar manner, but in so doing the saligenin is changed to saliretin.

Populin, the benzoyl derivative of salicin, $C_{13}H_{17}(C_7H_5O)O_7 + 2H_2O$, occurs in the bark and leaves of *Populus tremula.* It can also be artificially made by the action of benzoic anhydride upon salicin.

Helicin, Salicylaldehyde-glucose, $C_6H_4(O . C_6H_{11}O_5) . CHO$, is produced by oxidizing salicin with nitric acid. It reverts to salicin upon reduction. It can be artificially prepared from salicylic aldehyde and acetochlorhydrose. It is broken down just like salicin by ferments or dilute acids.

Glucose-cumaraldehyde, $C_6H_{11}O_5 . O . C_6H_4 . CH = CH . CHO$, and

Methylgluco-o-cumar-ketone result from the condensation of helicin with aldehyde and acetone (B. **24**, 3180).

4. **Amygdalin,** *Mandelo-nitrile diglucose,* $C_{20}H_{27}NO_{11} + 3H_2O : C_6H_5CH . CN$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | $
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O . C_{12}H_{21}O_{10}$,

occurs in bitter almonds and in the kernels of Pomaceæ and Amygdalaceæ, as well as in cherries, peaches, apricots, and the leaves of the cherry laurel. Amygdalin crystallizes from alcohol in white, shining leaflets, and dissolves readily in water and hot alcohol. On boiling with dilute acids, or upon standing with water and *emulsin*, an enzyme present in bitter almonds, amygdalin, is decomposed into *oil of bitter almonds,* dextrose, and *hydrocyanic acid.* When amygdalin is boiled with alkalies, the nitrogen is evolved as ammonia, and *amygdalic acid,* $C_{20}H_{28}O_{13}$, is produced; this decomposes into mandelic acid and glucoses, when boiled with dilute acids.

Yeast separates but one molecule of glucose from amygdalin, and there results **mandelnitrilo-** or **amygdonitriloglycoside,** $C_6H_5 . CH . CN$ O / OCH . [CHOH]$_2$. CH . CHOH . CH$_2$OH (the CH bonded to the lower OCH, the O bridging to the second CH), melting at 147–149°, which emulsin resolves into oil of bitter almonds, prussic acid, and glucose (B. **28**, 1508).

5. **Coniferine,** $C_{16}H_{22}O_8 + 2H_2O$, is found in the cambium of coniferous woods, in asparagus, and in the black root of *Scorzonera hispanica* (B. **25**, 3221). It effloresces in the air, and melts at 185°. It acquires a dark blue color when moistened with phenol and hydrochloric acid. Boiling acids or emulsin decompose it into glucoses and *Coniferyl Alcohol,* $C_6H_3\begin{pmatrix}O . CH_3\\OH\end{pmatrix} . C_3H_4 . OH$, which is oxidized by chromic acid to—

Glycovanillin, $C_6H_3(O . CH_3)(O . C_6H_{11}O_5) . CHO$, the glucoside of vanillin, melting at 192°. Acids or emulsin split it up into glucoses and vanillin (B. **18**, 1595, 1657).

Syringin, *Methoxyl-coniferine,* $C_{17}H_{24}O_9 + H_2O = C_6H_{11}O_5 . O . C_6H_2(OCH_3)_2C_3H_4OH$, occurs in the bark of *Syringia vulgaris* and *Ligustrum vulgare.* It melts at 191° and shows changes similar to those of coniferine.

6. **Phloridzin,** $C_{21}H_{24}O_{10}$, melting at 108°, occurs in the root-bark of various fruit trees; hence the name, from φλοίος, bark, and ῥίζα, root. It is intimately related to the pentosides: ***naringin*** and ***hesperidin.*** It breaks down into grape sugar and phloretin,

the phloroglucin ester of p-oxyhydratropic acid, and the latter into phloroglucin (p. 165) and phloretic acid (p. 226):

$$C_{21}H_{24}O_{10} + H_2O = C_6H_{12}O_6 \text{ (Glucose)} + C_{15}H_{14}O_5 \text{ (Phloretin)}$$
$$C_{15}H_{14}O_5 + H_2O = C_6H_6O_3 \text{ (Phloroglucin)} + C_9H_{10}O_3 \text{ (Phloretic Acid)}.$$

7. **Æsculin**, $C_{15}H_{16}O_9 + \frac{1}{2}H_2O$, melts at about 205° when it is anhydrous. It is found in the horse-chestnut, *Æsculus hippocastanum*, and in the root of the wild jasmine, *Gelsemium sempervirens*. Acids or ferments resolve it into glucose and æsculetine or 4,5-dioxycoumarin.

8. **Daphnin**, $C_{15}H_{16}O_9 + 2H_2O$, melting at 200°, is isomeric with the preceding. It is obtained from the bark of *Daphne alpina*. It breaks down into glucose and daphnetin or 3,5-dioxycoumarin (p. 283).

9. **Fraxin**, $C_{16}H_{18}O_{10}$, occurs in the bark of *Fraxinus excelsior*, and, like æsculin, in the bark of the horse-chestnut. It decomposes into glucose and fraxetin, the monomethyl ether of a trioxycoumarin (B. **27**, R. 130).

10. **Iridin**, $C_{24}H_{26}O_{13}$, melting at 208°, occurs in the root of the violet, *Iris florentina*, etc. Dilute sulphuric acid resolves it into grape sugar and irigenin, $C_{18}H_{16}O_8$. The latter is probably a polyoxyketone. Concentrated caustic alkali decomposes it into formic acid, an aromatic oxyacid,—*iridic acid*, $C_{10}H_{12}O_6$, melting at 118°, which by loss of CO_2 becomes **iridol** or 3-oxy-4,5-dimethoxy-1-methylbenzene, melting at 57°,—and *iretol*, $C_7H_8O_4$, or methoxyphloroglucin, melting at 186° (p. 165) (B. **26**, 2010; **27**, R. 514).

11. **Ruberythric Acid**, $C_{26}H_{28}O_{14} = HO \cdot C_{14}H_6O_2 \cdot O \cdot C_{12}H_{14}O_3(OH)_7$, melting at 258–260°, is the glucoside of alizarin (p. 427). It is formed in the madder root of *Rubia tinctorum*, and breaks down under the influence of hydrochloric acid into alizarin and glucose (B. **20**, 2244). Purpurin is also contained in the madder root as a glucoside.

12. **Digitalin** (*Digitalinum verum*, Kiliani), $C_{29}H_{46}O_{12}$, is an amorphous glucoside. It is the active principle of the digitalis glucosides, which occur in the leaves of *Digitalis purpurea* and *lutea*. Concentrated hydrochloric acid breaks it down into **digitaligenin**, $C_{16}H_{22}O_2$, grape sugar, $C_6H_{12}O_6$, and **digitalose**, $C_7H_{14}O_5$.

Its therapeutic action consists in its occasioning "less frequent but more satisfactory heart contractions."*

The chief ingredient of the digitalis glycosides is without therapeutic action. It is crystalline **digitonin**, $C_{27}H_{44}O_{13}$, which is resolved by aqueous alcoholic hydrochloric acid into **digitogenin**, $C_{15}H_{24}O_4$, glucose, and galactose. The decomposition of the latter has led to a series of acids, the constitution of which is as yet undetermined (B. **27**, R. 881; **28**, R. 1056).

13. **Saponin**, $C_{32}H_{54}O_{18}$, from the root of *Saponaria officinalis*, is a white amorphous powder, which provokes sneezing and foams in aqueous solutions. Its decomposition yields glucose and sapogenin, $C_{14}H_{22}O_2$.

14. **Convolvulin**, $C_{31}H_{50}O_{16}$, from the jalapa root of *Convolvulus purga*, is a gummy mass, which is a powerful purgative. Among its decomposition products are, in addition to a sugar, **d-Methyl-ethyl-acetic Acid**, and an **Oxypentadecylic Acid**, $C_2H_5CH(CH_3) \cdot CH(OH)C_9H_{18} \cdot CO_2H$, melting at 50°. Nitric acid oxidizes the latter to methyl-ethyl-acetic acid and an acid, $C_{10}H_{18}O_4$ (B. **27**, R. 885), melting at 116°, isomeric with sebacic acid (1, 455).

15. **Jalapin**, *scammonin*, $C_{34}H_{56}O_{16}$, from *Convolvulus orizabensis*, and from scammonium resin, yields acetic acid, tiglic acid, and palmitic acid upon distillation (B. **26**, R. 591; **27**, R. 736).

16. **Polygonin**, $C_{21}H_{20}O_5$, melting at 203°, is a glycoside, and has been obtained from the root-bark of *Polygonum cuspidatum*. It yields emodin when it is decomposed with alcoholic hydrochloric acid (B. **29**, R. 86).

Pentosides, Rhamnosides.—The following pentosides are to be regarded as ethereal compounds of *rhamnose*, $C_6H_{14}O_6 = C_6H_{12}O_5 + H_2O$ (1, 536), or of isodulcite:

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* Binz, "Grundzüge der Arzneimittellehre," p. 52.

1. **Naringin**, $C_{21}H_{26}O_{11} + 4H_2O$, melts when anhydrous at 170°. It is found chiefly in the blossoms and also in other parts of the tree *Citrus decumana* of Java. The name of the pentoside is derived from "naringi," a Sanscrit word meaning orange. Dilute acids decompose it into rhamnose and *naringenin*, melting at 230°. The latter is the phloroglucin ether of p-oxycinnamic acid, which concentrated caustic potash breaks down into phloroglucin (p. 165) and p-coumaric acid (p. 282) (B. **20**, 296):

$$C_{21}H_{26}O_{11} = C_6H_{14}O_6 \text{ (Rhamnose)} + C_{15}H_{12}O_5 \text{ (Naringenin)}$$
$$C_{15}H_{12}O_5 + H_2O = C_6H_6O_3 \text{ (Phloroglucin)} + C_9H_8O_3 \text{ (p-Coumaric Acid)}.$$

2. **Hesperidin**, $C_{22}H_{26}O_{12}$ (?), or $C_{50}H_{60}O_{22}$ (?), melting at 251°, is present in unripe oranges, lemons, etc. It decomposes, when heated, into glucose, rhamnose, and hesperetin, melting at 226°. Caustic potash resolves the latter into phloroglucin and isoferulic acid (p. 283) (B. **14**, 948):

$$C_{50}H_{60}O_{27} + 3H_2O = 2C_6H_{12}O_6 + C_6H_{14}O_6 \text{ (Rhamnose)} + 2C_{16}H_{14}O_6 \text{ (Hesperetin)}$$
$$C_{16}H_{14}O_6 + H_2O = C_6H_6O_3 \text{ (Phloroglucin)} + C_{10}H_{10}O_4 \text{ (Isoferulic Acid)}.$$

3. **Quercitrin**, $C_{21}H_{22}O_{12}$, is present in the bark of *Quercus tinctoria* and is applied under the name quercitrone as a yellow dye. It breaks down into rhamnose and quercetin (see this), a phenylbenzopyrene derivative (B. **26**, R. 234; **28**, 2303):

$$C_{21}H_{22}O_{12} + H_2O = C_6H_{14}O_6 \text{ (Rhamnose)} + C_{15}H_{60}O_7 \text{ (Quercetrin)}.$$

4. **Frangulin**, $C_{21}H_{20}O_9$, melting at 286°, occurs in the bark of *Rhamnus frangula*. When it is saponified with alcoholic hydrochloric acid rhamnose, *emodin* (p. 429) and a trioxymethylanthraquinone, isomeric with the latter, are produced (B. **25**, R. 370):

$$C_{21}H_{20}O_9 + 2H_2O = C_6H_{14}O_6 \text{ (Rhamnose)} + C_{15}H_{10}O_5 \text{ (Emodin)}.$$

BITTER PRINCIPLES.

Under the head of "bitter principles," or indifferent substances, is embraced a class of vegetable bodies many of which have already found their place in the chemical system. Those yet uninvestigated are:

Aloïn, $C_{17}H_{18}O_7$, or $C_{17}H_{16}O_7$ (?) (B. **23**, R. 207), found in aloes, the dried sap of many plants of the aloe variety. It forms fine needles, possesses a very bitter taste, and acts as a strong purgative. If digested with nitric acid it yields *aloetic acid*, $C_{14}H_4(NO_2)_4O_2$ (*tetranitroanthraquinone*) and chrysammic acid, *dioxytetranitroanthraquinone*, $C_{14}H_2(NO_2)_4(OH)_2$. Anthracene is formed when aloïn is heated with zinc-dust (B. **1**, 105). It forms *alorcinic acid*, $C_9H_{10}O_3 + H_2O$, when fused with caustic potash. This breaks down into orcin and acetic acid.

Cantharidin, $C_{10}H_{12}O_4$, melts at 218° and sublimes readily. It is contained in Spanish flies and other insects. It tastes very bitter and produces blisters on the skin. It dissolves when heated with alkalies and forms salts of *cantharinic acid*, $C_{10}H_{14}O_5$. It combines with phenylhydrazine to an *addition product*, $C_{16}H_{20}N_2OH$, melting at 194°, and a *phenylhydrazone*, melting at 238° (B. **26**, 140). Hydriodic acid converts cantharidin into *cantharic acid*, $C_{10}H_{12}O_4 = C_8H_{11}O . CO . CO_2H$, isomeric with it. When this acid is distilled with lime, *cantharene* or *dihydro-o-xylene* (p. 294) results.

Picrotoxin, $C_{15}H_{16}O_6 + H_2O$, is found in the grains of cockle, and crystallizes in fine needles, melting at 201°. It has an extremely bitter taste and is very poisonous. When digested with hydriodic acid it becomes **picrotoxic acid**, $C_{15}H_{18}O_4$ (B. **24**, R. 912), melting at 134°.

Santonin, $C_{15}H_{18}O_3$, melting at 170°, $[\alpha]_D = -171.37°$, is the active principle of worm-seed. It dissolves in alkalies to salts of **Santonic Acid**, $C_{15}H_{20}O_4$, which breaks down at 120° into water and santonin. On boiling with baryta-water we have formed salts of isomeric **santoic acid**, $C_{15}H_{20}O_4$, which melts at 171°.

This acid, upon further oxidation, yields a tetracarboxylic acid. For its constitution see B. **29**, R. 1119. Santonin is a lactone. It bears the same relation to santonic and santoic acids as coumarin to coumarinic and coumaric acids. Again, it contains the ketone group; its *phenylhydrazone* melts at 220°. When santonin is reduced with hydriodic acid or with stannous chloride and hydrochloric acid, *santous acid*, $C_{15}H_{20}O_3$, results. This is dextro-rotatory and melts at 179°. The corresponding lævorotatory modification and the (d + l)-acid are known. When these three acids are fused with caustic potash, propionic acid, dimethyl-β-naphthol, and hydrogen are produced. Hence it would seem that santonin is a derivative of a *hexahydrodimethylnaphthalene* (B. **27**, 530; **28**, R. 392; **29**, R. 291, 296). When santonin is reduced with tin and hydrochloric acid, not only santous acid is formed, but also a hydrocarbon, $C_{10}H_{13}(CH_3)_2$-(C_2H_5), boiling at 248°, which probably is dimethylethyloctohydronaphthalene (B. **28**, R. 622).

The conversion of santonin in acetic acid solution, in sunlight, into **photosantoic acid**, $C_{15}H_{22}O_5$, and in alcoholic solution into **photosantoic ethyl ether** (B. **18**, 2859), is remarkable.

NATURAL DYES.

The important natural dyes, *indigo*, *alizarin*, and its allies, *euxanthic acid*, *gentisin*, etc., have found their place in the system of organic chemistry. The following are some of the natural dyes which have not yet been investigated:

Brasilin, $C_{16}H_{14}O_5$, is found in Brazil-wood and red-wood; crystallizes with $1\frac{1}{2}H_2O$ in white, shining needles, and dissolves in alkalies with a carmine-red color on exposure to the air. Acids then precipitate *brasileïn*, $C_{16}H_{12}O_5 + H_2O$, from the solution. The action of iodine upon brasilin also produces this compound. It regenerates brasilin by reduction. When distilled, it yields resorcinol.

Brasilin forms mono-, di-, tri-, and tetra-alkyl ethers (B. **27**, 524; R. 304; **29**, R. 219).

Hæmatoxylin, $C_{16}H_{14}O_6 + 3H_2O$, the coloring matter of logwood (*Hæmatoxylon Campechianum*), is very soluble in water and alcohol, and crystallizes in yellowish prisms having a sweet taste. It dissolves in alkalies with a violet-blue color. When distilled or fused with potassium hydroxide, pyrogallic acid and resorcinol result from it. If the ammonium hydroxide solution be allowed to stand exposed to the air, there results **hæmateïn-ammonia**, $C_{16}H_{11}(NH_4)O_6$, from which acetic acid precipitates the free **hæmatin**, $C_{16}H_{12}O_6$ (at 120°), a reddish-brown body, which has metallic lustre after drying (A. **216**, 236). It yields penta-ethyl- and penta-acetyl ethers. The behavior of brasilin and hæmatoxylin seems to point to relations between these two bodies and the xanthone and fluorane derivatives (B. **22**, R. 558; **27**, R. 304; **29**, R. 219).

Carthamin, $C_{14}H_{16}O_7$, occurs in safflower, the blossoms of *Carthamus tinctorium*, and is precipitated from its soda solution by acetic acid as a dark red powder, which, on drying, acquires a metallic lustre. It dissolves with a beautiful red color in alcohol and the alkalies. It yields para-oxybenzoic acid with caustic potash (A. **136**, 117).

Curcumin, $C_{14}H_{14}O_4$, the coloring-matter of turmeric root, from *Curcuma longa* and *viridiflora*, crystallizes in orange-yellow prisms, melts at 177°, and dissolves in the alkalies to brownish-red salts. Ethyl vanillic acid is obtained on oxidizing diethylcurcumin with potassium permanganate (B. **17**, R. 332).

Luteolin, Maclurin, see p. 228.

Litmus, see p. 162.

Usninic Acid, Lichen Substances, etc.—A. **295**, 222; B. **30**, 357.

Carminic Acid, $C_{11}H_{12}O_7$, is found in cochineal, from *Coccus cacti coccinellifери*, an insect peculiar to different cactus varieties. It is a purple-red mass, dissolving readily in water and alcohol, which forms red salts with the alkalies. Boiling nitric acid converts it into *nitrococcic acid* (p. 226). Bromine converts carminic acid into two bromides, a tribromide (β) and a tetrabromide (α), which by further decomposition yield *methyl-*

dibromoxyphthalic acid, $HO[4]C_6[3,5]Br_2[6]CH_3[1,2](CO_2H)_2$. The *β-bromide* is probably an *a*-napthoquinone derivative, and carminic acid the hydrate of a methyldioxy-*a*-naphthoquinone (p. 405) (B. **26**, 2647; **27**, 2989).

Potassium persulphate oxidizes the cochineal dye to two acids, which can be separated by their varying solubility in water. They are *cochenillic acid* and *coccinic acid*. Bromine converts the first into tribromcresotinic acid (B. **30**, 690). Cochineal is applied in wool-dyeing for the production of scarlet-red colors. This application has diminished very greatly since the discovery of the red azo-dyes, like *Biebrich scarlet* and others.

Chlorophyl, *Leaf Green*, occurs in all the green parts of plants and in the chlorophyl granules, which also contain wax and other substances. The composition of chlorophyl has not yet been established. There appears to be some iron in it. See A. **284**, 81, for the decomposition of chlorophyl with alkalies and acids. It is rather remarkable that chlorophyl substances yield pyrrol when they are distilled with zinc-dust, hence they appear to be intimately related to this substance. This observation was also made with the blood substances (1, 585). The hæmatoporphyrin obtained from the latter shows great similarity in absorption spectra to the phylloporphyrin from chlorophyl, so that there seems to be some connection in the constitution of blood and vegetable dyestuffs (B. **29**, 1766; R. 415).

III. HETEROCYCLIC COMPOUNDS.

The carbocyclic substances treated in the preceding section belong to the class of isocyclic compounds which consist of rings of atoms of one and the same element. Apparently, very few elements are adapted to such a ring-formation.*

However, substances are known in great number and complexity which are based upon ring-skeletons consisting of atoms of various elements. These bodies have been arranged under the designation "*heterocyclic compounds.*" It is true that a series of inorganic bodies† can be included in this category, but it is our purpose to consider only the "organo-inorganic"—*i. e.*, those ring-systems the members of which are formed from carbon in union with other elements, most important of which are oxygen, sulphur, but especially nitrogen. In many cases sulphur can be replaced by selenium, and there are some substances known in which phosphorus forms a ring with C-atoms.‡

From the standpoint of organic chemistry, the basal element of these rings is carbon, and accordingly the members not produced by C-atoms are designated as *hetero-atoms*, and distinguished as *mono-*, *di-*, *tri-*, *tetra-*, etc., hetero-atomic rings, depending upon whether one, two, three, four, or more hetero-atoms have participated in their formation. To express the number of atoms constituting the entire ring, the rings are termed *three*, *four*, *five*, *six*, and *poly-membered rings.*

Many heterocyclic compounds have been discussed in the preceding chapters—for example, the *cyclic ethers of the glycols and thioglycols,* like ethylene oxide, diethylene dioxide, diethylene disulphide; the *cyclic alkylenimides,* like tetramethyleneimide or pyrrolidine, diethylenediimide, or piperazine; the *cyclic esters of oxy- and amido-acids*, like the lactides, the lactones, the lactams; the *cyclic derivatives of dibasic carboxylic acids*, like anhydrides, imides, alkylen esters, alkylenamides, etc. (see I, 313; ring-shaped compounds). These bodies attached themselves, as their names indicate, naturally to known classes of compounds with open chains. They can be readily obtained from substances with open chains and be equally readily changed back into them. In the succeeding sections, however, a series of heterocyclic bodies will be described which manifest

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* Nitrogen, mainly, in addition to carbon. The allotropic modifications of many elements are probably induced by the formation of isocyclic rings—*e.g.*, that of oxygen in ozone, O_3, and that of sulphur in the molecular weight, S_8, etc.

† See Bischoff, "Handbuch der Stereochemie," p. 641.

‡ Finally, rings are present in the salts of dicarboxylic acids, sulphocarbonic acids, disulphonic acids, glycols, etc., containing bi- and polyvalent metals. Members are formed by the metal atoms.

varying deportment in so far that the rings upon which they are constructed can not be resolved in a simple way. Such rings are rather nuclei to which derivatives attach themselves which are related to the fundamental substances, the same as the aromatic substances are related to benzene. Usually, these substances, like benzene, contain unsaturated unions.

It has, therefore, been assumed that in these rings, as in benzene, there is a particular kind of linkage—"potential valences" (see p. 41 and B. **24**, 1761). These explain the stability of these bodies. If the potential valences are dissolved by the addition of hydrogen or some such substance, then saturated bodies result; these possess the "alicyclic character" (see p. 18), and so far as their decomposability is concerned, they in the main exhibit the character of the heterocyclic substances discussed after the fatty bodies. A real fundamental difference, however, between the two rings just described does not exist. Compounds were studied in connection with the lactones and dibasic anhydrides which offered great resistance to decomposition by water absorption, etc. (see I, 379 462, 465). On the other hand, there are many bodies in which potential linkages are assumed which are very easily decomposed by certain reagents—*e. g.*, pyrrol by hydroxylamine yielding succinaldehyde-dioxime (I, 327), and glyoxaline by benzoyl chloride and sodium, forming dibenzoyldiamidoethylene, etc.

The heterocyclic rings containing five and six members are, like the analogous carbon rings, the most stable and important. They will be treated in this section. The tendency to the formation of six-membered rings is shown also in the processes of *polymerization;* formaldehyde, by the coalition of three molecules, becomes six-membered trioxymethylene; acetaldehyde becomes the six-membered paraldehyde, and the cyanogen compounds polymerize to derivatives of a six-membered ring, consisting of 3 C- and 3 N-atoms, etc. (compare also the aromatic polymerization, p. 43). Three- and four-membered rings are usually formed with extreme difficulty, and are easily torn asunder (p. 443). The seven-membered rings are not well known, and are also unstable (B. **27**, 2902; **28**, R. 756). Special mention may be made of substances like *diphenic anhydride* and *diphenimide*, which contain seven-membered rings (p. 341). Individual compounds are known in which heterocyclic rings are assumed to be present which contain eight or more members.

Eight-membered rings are present in the condensation product of o_2-diamidodiphenyl and benzil (B. **26**, 1704): $\begin{array}{l} C_6H_5C = N - C_6H_4 \\ \quad | \\ C_6H_5C = N - C_6H_4 \end{array}$, melting at 238°. Upon reduction this yields a *tetrahydro derivative*, a base, melting at 154°.

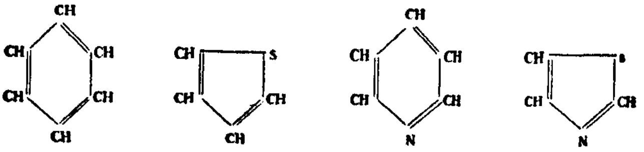
Diphenhomazine (p. 347), $C_6H_4{<}\begin{array}{l} N = C(C_6H_5) \\ C(C_6H_5) = N \end{array}{>}C_6H_4$, results from the condensation of two molecules of o-amidobenzophenone; and, finally, the cyclic alkylen esters of the succinic acid series (A. **280**, 169); compare—

Hydrazioxalyl, $\begin{array}{l} CO - NH - NH - CO \\ | \qquad\qquad\qquad\quad | \\ CO - NH - NH - CO \end{array}$ (B. **29**, R. 180). It is probable that a 13-membered ring is present in cycloformazyl formic ester,

$CO_2R \,.\, C{<}\begin{array}{l} N \,.\, NH[4]C_6H_4 \\ \qquad\qquad\quad | \\ N : \;\; N[4]C_6H_4 \end{array}$ (p. 339), and a sixteen-membered ring in tetrasalicylide (p. 225).

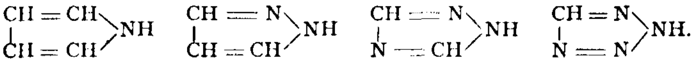
Consideration in the sense of A. v. Baeyer's strain theory (p. 19) is rendered difficult

by the varying nature of the hetero-atoms entering into the composition of the ring. Certain facts most certainly contribute to the representation of the spacial relations of many of the hetero atoms. Thiophene, with a ring of four CH-groups and one S-atom, very greatly resembles benzene, containing six CH-groups. Thiazole, consisting of three CH-groups, one N-atom, and one S-atom, similarly resembles pyridine, which has five CH-groups and one N-atom. It would therefore seem that a sulphur atom is capable of replacing the bivalent group —CH = CH— in the ring:



Benzene Thiophene Pyridine Thiazole.

It is an almost universal rule that an N-atom can replace a methine group in a ring without causing any essential loosening of the ring-union. If we suppose a methine group in benzene to be replaced by N, the product will be pyridine, which is about as stable a ring as we have in benzene. And if the methine groups in pyrrol be successively replaced by one, two, and three N-atoms, there also results a series of derivatives in which ring-stability is very evident:



Pyrrol Pyrazole Pyrrodiazole Tetrazole.

A general review of the many heterocyclic ring systems can be obtained from two points of view. *Homologous series* are obtained by arranging together the rings with similar hetero-atoms according to the increasing number of C-members. The following series of rings have been deduced in this way:

(a) WITH AN O-MEMBER.

: C——C : (—O—)	: C—C—C : (—O—)	: C—C—C—C : (—O—)	: C—C—C—C—C : (—O—)
H_2C——CH_2 (—O—) Ethylene Oxide	H_2C—CH_2—CH_2 (—O—) Trimethylene Oxide	H_2C—CH_2—CH_2—CH_2 (—O—) Tetramethylene Oxide	H_2C—CH_2—CH_2—CH_2—CH_2 (—O—) Pentamethylene Oxide
—	—	H_2C—CH_2—CH_2—CO (—O—) Butyrolactone	H_2C—CH_2—CH_2—CH_2—CO (—O—) Valerolactone
—	—	OC—CH_2—CH_2—CO (—O—) Succinic Anhydride	OC—CH_2—CH_2—CH_2—CO (—O—) Glutaric Anhydride
—	—	HC = CH—CH = CH (—O—) Furfurane	HC = CH—CO—CH = CH (—O—) Pyrone

(b) WITH AN S-MEMBER.

: C——C : S	: C—$\ddot{\text{C}}$—C : S	: C—$\ddot{\text{C}}$—$\ddot{\text{C}}$—C : S	: C—$\ddot{\text{C}}$—$\ddot{\text{C}}$—$\ddot{\text{C}}$—C : S
H_2C—CH_2 S [Ethylene Sulphide]	H_2C—CH_2—CH_2 S [Trimethylene Sulphide]	COOH . CH—CH_2—CH_2—CH . COOH S Tetrahydrothiophene-dicarboxylic Acid	—
—	—	CO—CH_2—CH_2—CO S Sulphosuccinyl	—
—	—	CH = CH—CH = CH S Thiophene	CH=CH—CH_2—C$(CH)_3$=CH S Methylpenthiophene

(c) WITH AN N-MEMBER.

: C——C : $\dot{\text{N}}$	: C—$\ddot{\text{C}}$—C : $\dot{\text{N}}$	: C—$\ddot{\text{C}}$—$\ddot{\text{C}}$—C : $\dot{\text{N}}$	: C—$\ddot{\text{C}}$—$\ddot{\text{C}}$—$\ddot{\text{C}}$—C : $\dot{\text{N}}$
CH_2—CH_2 NH [Ethyleneimide]	CH_2—CH_2—CH_2 NH Trimethyleneimide	CH_2—CH_2—CH_2—CH_2 NH Tetramethyleneimide Pyrrolidine	CH_2—CH_2—CH_2—CH_2—CH_2 NH Pentamethyleneimide Piperidine
—	—	CH_2—CH_2—CH_2—CO NH Butyrolactam	CH_2—CH_2—CH_2—CH_2—CO NH Valerolactam
OC — CO NH Oxalimide	—	OC—CH_2—CH_2—CO NH Succinimide	OC—CH_2—CH_2—CH_2—CO NH Glutarimide
—	—	CH = CH—CH = CH NH Pyrrol	CH—CH = CH—CH = CH N Pyridine

Complication by virtue of isomerides arises in the case of rings having two hetero-atoms. These isomerides are occasioned by the varying positions of the hetero-atoms with reference to one another—*e. g.* : *

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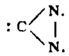
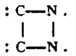
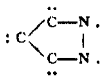
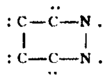
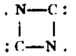
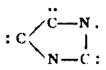
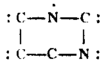
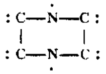
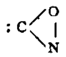
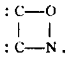
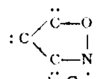
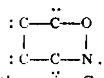
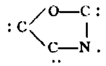
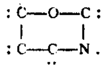
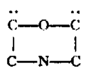
* In the following paragraphs the individual ring-types are represented in diagram to save space. The valences remaining free in the case of the different atoms after the ring-formation are indicated by dots, and the most important compounds or classes of compounds are arranged under the various rubrics to which they belong.

RINGS WITH TWO N-MEMBERS.

 Hydrazi Compounds, Diazomethane	 Dimethylaziethane	 Pyrazole Group	 Pyridazine Group
—	 Ethidene Urea, Dicyan-compounds	 Glyoxaline Group, Cyclic Ureas	 Pyrimidine Group, Cyclic Ureas
—	—	—	 Pyrazine Group, Diethylene-diimide

RINGS WITH AN O- AND AN N-MEMBER.

 β-Benzaldoxime Ether	 Betaïne	 Isoxazole Group	 Orthoxazine Group
—	—	 Oxazole Group	 Metoxazine Group, Pentoxazoline
—	—	—	 Paroxazine Group

The three- and four-membered systems naturally disappear in the series of rings having three and four hetero-atoms. The branching of the series in consequence of position-isomerides with the hetero-atoms becomes more frequent, so that the relations dependent upon homology frequently become obscure. In the monohetero-atomic rings also the homology usually appears solely in the case of the saturated (alicyclic) ring-systems, whereas the more important unsaturated systems, with more pronounced aromatic character, show at times very varying deportment—

e.g., when in the homologous series with an N-member the group of the five-membered pyrrol comes into juxtaposition with that of the six-membered pyridine, although the representatives of these two groups manifest very great differences in their behavior.

Hence it is more practical to group the ring systems according to the number of members composing the ring. In this manner only systems of rings of approximately like stability will come together, and they will, therefore, very probably yield similar derivatives. Hence to groups of three rings will be attached such as have four, five, six, etc., members. Each of these groups will have subdivisions in accordance with the number of hetero-atoms, so that, for example, in the group of five-membered heterocyclic rings there will be discussed first the monohetero-atomic, then the di-, tri-, and tetrahetero-atomic systems. This might be called grouping according to *isologous series* :

THREE-MEMBERED HETEROCYCLIC SUBSTANCES.

: C——C : \O/ Ethylene Oxide	: C——C : \S/ [Ethylene Sulphide]	: C——C : \N/ [Ethyleneimide] Oxalimide
: C——N. \O/ *β*-Benzaldoxime Ether	: C——N. \S/ Thialdolaniline (p. 79)	: C——N. \N/ Diazomethane, Hydrazi-compounds

FOUR-MEMBERED HETEROCYCLIC SUBSTANCES.

: C—C̈—C : \O/ Trimethylene Oxide	: C—C̈—C : \S/ —	: C—C̈—C : \N/ Trimethyleneimide
: C—C̈—N . \O/ Betaïne	: C—C̈—O \S/ Thetine	: C—C̈—N . \N/ Dimethylaziethane
—	: C—Ṅ—C : \S/ Alkylidene-*ψ*-thioureas	: C—Ṅ—C : \N/ Alkylidene Ureas, Dicyanogen Compounds (?)

FIVE-MEMBERED HETEROCYCLIC SUBSTANCES.

: C—C—C—C : O *Furfurane*, γ-Lactones, Succinic Anhydride	: C—C—C—C : S *Thiophene*, Sulphosuccinyl	: C—C—C—C : Se Selenophene	: C—C—C—C : N *Pyrrol*, γ-Lactams, Succinimide
: C—C—C—N . O *Isoxazole* Group	: C—C—C—N . S Isobenzothiazole	—	: C—C—C—N . N *Pyrazole* Group
: C—C—O—C : O Cyclic Ethers and Esters of Glycol, Aldehyde, Carbonic Acid, and Oxalic Acid	: C—C—S—C : S Ethidene-ethylene Disulphide	—	
: C—C—N—C : O *Oxazole* Group	: C—C—N—C : S *Thiazole* Group	: C—C—N—C : Se Selenazole Group	: C—C—N—C : N *Glyoxaline* Group, Cyclic Ureas
: C—C—N—N O Diazo-oxides	: C—C—N—N S Diazosulphides	: C—C—N—N Se Diazoselenide	: C—C—N—N N *Osotriazole* Group, Azimides
. N—C—C—N . O Furazane Group	. N—C—C—N . S Piazthioles	. N—C—C—N . Se Piaselenoles	
: C—N—C—N . O Azoximes	: C—N—C—N . S Azosulphimes	—	: C—N—N—C : N *Triazole* Group
: C—N—N—C : O *Oxybiazole* Group	: C—N—N—C : S *Thiobiazole* Group	—	
—	. N—C—N—N . S Triazsulpholes	—	: C—N—N—N . N *Tetrazole* Group

SIX-MEMBERED HETEROCYCLIC SUBSTANCES.

: C—C—C—C—C : O Pentamethylene Oxide, δ-Lactones, Glutaric Acid Anhydride. *Pyrone* Group.	: C—C—C—C—C : S *Penthiophene* Group	: C—C—C—C—C : N Pentamethylene-imide (Piperidine). δ-Lactams, Glutarimide. *Pyridine* Group.
. C—C—C—C—N . O Carboxyl-oxime Anhydrides	—	. C—C—C—C—N . N *Pyridazine* Group
: C—C—C—O—C : O Cyclic Ethers and Esters of Trimethylene Glycol, Aldehyde, Carbonic Acid, Malonic Acid, etc.	: C—C—C—S—C : S Tetramethylene Disulphides	: C—C—C—N—C : N *Pyrimidine* Group
C—C—C—N—C : O *Pentoxazoline* Group	: C—C—C—N—C : S *Penthiazoline* Group	
: C—C—O—C—C : O Diethylene Oxide, Cyclic Anhydrides of α-Oxyacids	: C—C—S—C—C : S Diethylene Disulphide	: C—C—N—C—C : N *Pyrazine* Group
: C—C—N—C—C : O *Paroxazine* Group	: C—C—N—C—C : S *Parathiazine* Group	
: C—C—S—C—C : O Thio-diglycollic Anhydride		
. N—C—C—C—N . O Azoxazine Derivatives		. N—C—C—C—N . N *Osotriazine* Derivatives
: C—N—C—C—N . O Benzenylamidoxime Acetic Anhydride	: C—C—C—N—N . S Diazthine Derivatives	: C—N—C—C—N . N Unsym.-*Triazine* Group
: C—O—C—O—C : O Polymeric Aldehyde	: C—S—C—S—C : S Trithioaldehyde	: C—N—C—N—C : N Polymeric Cyanogen Compounds, *Cyanidine* Group
O—N—C—C—N . O Glyoxime-hyperoxide	—	. N—N—C—C—N . N *Osotetrazones*, *Phentetrazines*
		: C—N—N—C—N . N *Tetrazine* Group

Just as indene, naphthalene, anthracene, etc., are derived from benzene, so numerous di- and polycyclic, *condensed* nuclei are obtained from the heterocyclic rings that contain adjacent C-members. This is possible by the fact that the two adjacent C-members participate also in the formation of aromatic rings, like benzene, naphthalene, phenanthrene, etc. These condensed nuclei unite, as a rule, the properties of the carbocyclic with those of the heterocyclic ring. When definite names are not assigned them, as in the indol and quinoline groups, they are designated with the prefixes benzo- or phen-, dibenzo- or diphen-, naphtho-, etc., before the name of the heterocyclic ring.

Quite frequently substances having such condensed nuclei have the heterocyclic ring ruptured, and are then changed to ortho-substitution products of the carbon ring. Again, the heterocyclic ring shows itself more stable toward oxidizing agents, so that it is possible, by means of potassium permanganate, etc., to oxidize the condensed nuclei with destruction of the carbon ring and the production of ortho-dicarboxylic acids of the heterocyclic rings. Thus, acridine yields quinoline dicarboxylic acid, quinoline a pyridine dicarboxylic acid, benzoglyoxaline a glyoxaline-dicarboxylic acid, benzotriazole a triazole dicarboxylic acid, and phenazone a pyridine tetracarboxylic acid, etc.

Both the simple and condensed heterocyclic compounds have, as a rule, been made by the inner condensation of suitable fatty or fatty-aromatic bodies having open chains. Very often the intermediate products, leading directly to the ring, cannot be fixed because of their great inclination to the ring-formation; orthosubstitution products of benzene and naphthalene (pp. 38, 390) are especially well adapted for the production of condensed heterocyclic nuclei. They have afforded the starting-out material for the preparation of an immense number of substances belonging in this group.*

Many heterocyclic bodies also occur in technical and natural products. The large and important family of vegetable alkaloids belongs in the group of *pyridine* and the hydropyridines. *Pyridines* and *pyrrols* occur in coal-tar and bone-tar. *Thiophene* and *coumarone* are also present in coal-tar. *Furfurol* and other derivatives of furfurane have been found in the tar from wood. The important vegetable dye, *indigo,* and its allied bodies, are derivatives of indol. Many heterocyclic bodies prepared synthetically have been manufactured upon a technical scale, because of their coloring and therapeutic properties. This is true of the dyes of the *paroxazine*, *parathiazine*, and *paradiazine*-series, *e. g.*, *resorufin*, *methylene blue*, *toluylene red*, *safranine*, etc.; the dyes of the *thiazole-group*, and also of the important febrifuges, like *antipyrine*, *salipyrine*, *tolypyrine*, belonging to the pyrazole-group, and *piperazine* or hexa-hydropyrazine, etc.

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* Compare Kühling, "Stickstoffhaltige Orthocondensationsproducte," 1893.

1. THREE-MEMBERED HETEROCYCLIC COMPOUNDS.

As a rule, bodies of this class manifest "ring-strain" to a greater degree than the carbocyclic substances of the trimethylene series. That is, they are inclined, in consequence of a rupture of the ring, to take on additional atoms or atom groups. Hence, they are produced only under the most favorable conditions, and many compounds which formerly were regarded as based upon three-membered heterocyclic rings have, as a result of more recent study and investigation, had their formulas doubled, or have been discovered to be still higher steps in polymerization; compare *ethyleneimide, glycolide,* etc.

A. MONOHETEROATOMIC THREE-MEMBERED RINGS.

(a) Having an O-member: **Ethylene Oxide,** $\left.\begin{array}{l}H_2C\\ \;|\\ H_2C\end{array}\right>O$. The method of preparing this compound and its properties have already been described in connection with glycol of the aliphatic series (I, 298). It exhibits a great inclination toward a rupture of the ring. This is shown by the fact that it precipitates the hydroxides from solutions of the metals with the simultaneous formation of glycolacidylhydrins. The same tendency is observed with the substituted ethylene oxides, like *tetramethylethylene oxide* (I, 299), the *glycide derivatives* (I, 476; II, 256), condensed nuclei containing the ring of ethylene oxide—*e. g., tetrahydronaphthylene oxide* (p. 413) and *diketotetrahydronaphthylene oxide* (p. 413), etc.

(b) Having an S-member: *Ethylene Sulphide,* $\left.\begin{array}{l}H_2C\\ \;|\\ H_2C\end{array}\right>S$, corresponding to ethylene oxide, is apparently not capable of existing. It is usually its polymerides which are obtained: $(C_2H_4S)x$ and $(C_2H_4S)_2$ diethylene disulphide (I, 305); compare *Tolane Sulphide,* $\left.\begin{array}{l}C_6H_5C\\ \;\;\;|\\ C_6H_5C\end{array}\right>S$ (p. 375). See also the addition products of sulphur with ethylene and acetylene derivatives—B. 28, 1635; 30, 110.

(c) Having an N-member: *Ethylene Imide,* $\left.\begin{array}{l}H_2C\\ \;|\\ H_2C\end{array}\right>NH$, also appears unstable. Ethylene diamine hydrochloride and others rather yield the six-membered ring of piperazine (I, 314). It is assumed that oxalimide, $\left.\begin{array}{l}CO\\ |\\ CO\end{array}\right>NH$ (I, 436), as well as the *lactimides,—e. g.,* benzoyl-amido-cinnamic acid lactimide, $\left.\begin{array}{l}C_6H_5CH:C\\ \;\;\;\;\;\;\;\;\;\;\;\;\;\;|\\ \;\;\;\;\;\;\;\;\;\;\;\;OC\end{array}\right>NCOC_6H_5$ (p. 276),—contain a three-membered ring consisting of two C-atoms and one N-atom.

B. DIHETEROATOMIC THREE-MEMBERED RINGS.

Rings, consisting of C, N, and O, are assumed to be present in the nitrogen ethers of some of the aldoximes—*e. g.,* the n-alkyl benzaldoximes, $\left.\begin{array}{l}\;\;\;\;\;\;\;\;RN\\ \;\;\;\;\;\;\;\;\;|\\ C_6H_5.CH\end{array}\right>O$ (p. 185), which are resolved by acids into benzaldehyde and n-alkylhydroxylamines. The same

ring occurs in different polycyclic substances,—*e. g.*, the isatogen compounds,—such as **isatogenic acid**, $C_6H_4\langle{}^{CO-C\,.\,COOH}_{N\,=\,O}$ (p. 284), and in the products obtained by reducing acidylated o-nitranilines with ammonium sulphide—*e. g.*, $C_6H_4\langle{}^{NH-CCH_3}_{N\,=\,O}$ (see benzimide azole), etc. Compare also anthranil and anthroxan aldehydes (pp. 211, 250). Thialdolaniline, $C_6H_5N\!-\!CH\!-\!CH(OH)\,.\,CH_3$ (with $-S-$ closing the ring), contains a ring consisting of C, N, and S. The same may be observed of similarly formed compounds (see Usèbe's green, p. 359).

Hydrazi- and Azimethylene-group : Substances consisting of two N- and one C-atom are much better known. The hydrazi-derivatives belong in this class. They are obtained from the hypothetical *hydrazimethylene*, ${}^{NH}_{NH}\!>\!CH_2$ (Curtius, J. pr. Ch. [2], 44, 169, 554). They are produced in the action of hydrazine upon o-diketones and α-ketone carboxylic esters (1, 328)—*e. g.*, benzil, diacetyl, pyroracemic ester:

Benzoylphenylhydrazimethylene, $C_6H_5\,.\,CO\,.\,C(C_6H_5)\langle{}^{NH}_{NH}$, melts with decomposition at 151°, and **diphenyldihydrazimethylene**, ${}^{HN}_{HN}\!>\!C(C_6H_5)\,.\,C(C_6H_5)\langle{}^{NH}_{NH}$, melts at 147°. *Carboxylic Acids* of this result from the reduction of esters of the diazo-fatty acids:

Hydraziacetic Acid, ${}^{HN}_{HN}\!>\!CH\,.\,COOH$ (1, 366), and **Hydrazi-propionic Methyl Ester**, ${}^{HN}_{HN}\!>\!C(CH_3)\,.\,COOCH_3$, melting at 82°. The potassium salt of a **sulphohydraziacetic ester**, ${}^{HN}_{KO_3SN}\!>\!CH\,.\,CO_2C_2H_5$, has been made by the action of potassium sulphite upon diazoacetic ester (B. 28, 1848).

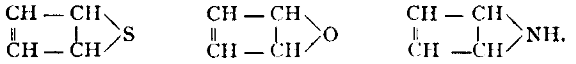
The hydrazi-compounds are readily changed by oxidation to the azi-derivatives containing two atoms less of hydrogen. They evolve nitrogen on the application of heat. See l. c. for other rearrangements. **Benzhydrazoïn**, ${}^{C_6H_5N}_{C_6H_5N}\!>\!CH\,.\,C_6H_5$ (p. 185), formed from benzaldehyde and hydrazobenzene, is a triphenyl hydrazimethylene.

The diazo-compounds of the aliphatic series are obtained from **azimethylene** or **diazomethane**. The latter is produced when nitrosomethylurethane is digested with methyl alcoholic potash. Compare vol. 1, 206, for its properties. It also results from the reduction of methyl nitramine (1, 171; B. 29, 961), and from the action of hydroxylamine upon methylchloramine (1, 169; B. 28, 1682).

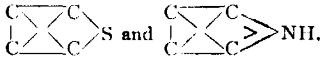
Diazo-acetic ester (1, 365), **diazopropionic ester** (1, 371), **diazosuccinic ester** (1, 501), and **diazomethane disulphonic acid**, ${}^{N}_{N}\!\!>\!C(SO_3H)_2$ (1, 405), are derivatives of diazomethane.

These bodies constitute the transition to the isocyclic ring of the diazoimide or hydrazoic acid, ${}^{N}_{N}\!\!>\!NH$.

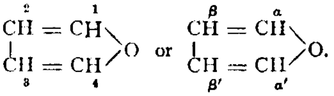
These syntheses harmonize with the accepted structural formulas for furfurane, pyrrol, and thiophene. However, experiments upon the refractive power of thiophene render probable the presence of but one double linkage in this compound (B. **20**, R. 103). A similar result was indicated by the heat of combustion of thiophene (B. **18**, 1832). Hence the following formulas have been proposed for thiophene, and for the analogous furfurane and pyrrol:



Many of the methods employed in making pyrrol derivatives and the ready transition, under the influence of oxidants, of all three groups of substances into derivatives of maleïc acid (see pp. 450, 454, 458) accord very well with these formulas. See B. **24**, 1447, 1758, for formulas like



To distinguish the possible isomerides the replaceable hydrogen atoms of the methine groups in furfurane, thiophene, and pyrrol are designated by numbers or letters, as with benzene:



The positions 1 and 4 are equal in value; also 2 and 3. The first are also termed α-, the latter β-positions. It is obvious that the mono-derivatives of furfurane, thiophene, and pyrrol can exist in two isomeric forms (α-derivatives and β-derivatives).

1. THE FURFURANE GROUP.*

Furfurane, Furane, C_4H_4O, boiling at 32°, was first obtained by distilling barium pyromucate (p. 451) (Limpricht, 1870; C. 1897, II, 268): ($C_4H_3O.CO_2H = C_4H_4O + CO_2$). It is present in the distillation products of pine wood. It is a liquid, insoluble in water, and has a peculiar odor. Metallic sodium has no effect upon it, nor does it combine with phenylhydrazine. It yields dye substances with isatin and phenanthraquinone (see above). It reacts very violently with hydrochloric acid, and forms a brown amorphous substance (like pyrrol red, p. 457). A pine shaving moistened with hydrochloric acid assumes a green color when brought in contact with the vapors of furfurane.

Brominated derivatives can be obtained from brom-pyromucic acids, or by the direct action of bromine upon furfurane. Addition products result from an excess of bromine.

See C. 1897, I, 1023, for **nitro-** and **amido-furfurane.**

Methyl Furfurane, $C_4H_3(CH_3)O$, is in all probability *sylvan*, which occurs in pine tar oil. It boils at 63° (B. **13**, 879).

α,α_1-**Dimethyl Furfurane,** $C_4H_2(CH_3)_2O$, is formed by the distillation of carbopyrotritartaric acid (p. 451), and has been synthesized from acetonyl acetone upon heating it with $ZnCl_2$ or P_2O_5. It boils at 94°.

* Compare "Das Furfuran, etc.," von A. Bender, 1889.

It regenerates acetonyl acetone when it is heated with dilute hydrochloric acid to 170°.

a,a_1-Phenyl-methyl Furfurane, $C_4H_2\left\{\begin{matrix}CH_3\\C_6H_5\end{matrix}\right\}O$, is produced from acetophenone-acetone (B. 17, 915 and 2759). It melts at 42° and boils at 235–240° C. Sodium, in alcoholic solution, converts it into a **tetrahydro**-compound.

Diphenyl Furfurane, melting at 91°, is obtained from diphenacyl (B. 23, R. 743; 26, 1447). **Triphenyl Furfurane**, melting at 93°, is formed from desylacetophenone (B. 21, 2933; 26, 61). **Tetraphenyl Furfurane, Lepidene** (B. 22, 2880), melting at 175°, is produced, together with benzil, when benzoin is heated with hydrochloric acid to 130° (p. 380).

Furfuro-stilbene, $C_4H_3O-CH=CH-C_4H_3O$, melting at 101°, is the stilbene of the furfurane series. It results upon heating polymeric thiofurfurol (B. 24, 3591).

Furfuryl Alcohol, $C_4H_3O.CH_2OH$, is a colorless syrup, which is colored green by hydrochloric acid. It results from the action of sodium amalgam and acetic acid upon the aldehyde furfurol, but more easily by treatment with aqueous caustic potash (B. 19, 2154). Furfurane carboxylic acid is produced at the same time ($2C_4H_3O.CHO + H_2O = C_4H_3O.CH_2OH + C_4H_3O.CO_2H$) (B. 19, 2154).

Furfuryl Methyl Ether, $(C_4H_3O).CH_2.O.CH_3$, boils at 134–136° (B. 26, R. 239).

Furfurylamine, $C_4H_3O.CH_2.NH_2$, boiling at 146°, results in the reduction of furfuronitrile (p. 450) and furfurol hydrazone (see below).

a-**Furfurol**, or **Furol**, $C_5H_4O_2 = C_4H_3O.CHO$, boiling at 162°, with the sp. gr. 1.163, is the aldehyde of pyromucic acid, and is produced in the distillation of bran (*furfur*, Fownes, 1849), or of sugar (Döbereiner, 1831), and wood, as well as most carbohydrates and glucosides, with dilute sulphuric acid. When present in even the merest traces it can be detected by the red coloration given by aniline or xylidine (B. 20, 541).

Furfurol is produced quantitatively when pentoses like arabinose, etc., are distilled with hydrochloric acid. Various analytical methods for the estimation of the pentoses are based on this fact (1, 536) (B. 28, R. 629). Glucuronic acid, when heated with hydrochloric acid, breaks down into furfurol, water, and CO_2 (B. 29, R. 280).

Furfurol is a colorless liquid with an aromatic odor. It is fairly soluble in water and very soluble in alcohol. It becomes brown on exposure to the air, and shows all the properties of an aldehyde. It combines with bisulphites, passes into furfuryl alcohol under the influence of sodium amalgam, and is changed to pyromucic acid by argentic oxide, and to the alcohol and acid through the action of caustic potash. It yields **furfuraldoxime** with hydroxylamine; this melts at 89° and boils at 205°. It unites similarly with phenylhydrazine, forming a *hydrazone*, melting at 96°. With orthoformic ester it yields the *acetal*, $C_4H_3O.CH(OC_2H_5)_2$, boiling at 187–190° (B. 29, 1008).

Furthermore, furfurol manifests *all the condensation reactions of benzaldehyde* (see below). (1) It combines with dimethylaniline to form a green dye-stuff, corresponding to malachite green. (2) It condenses with aldehydes and ketones of the fatty series to furfurane aldehydes and ketones with unsaturated side-chains. This reaction occurs quite readily on digesting with dilute caustic soda (B. 13, 2342). Thus, with acetaldehyde it forms **Furfur-acroleïn**, $C_4H_3O.CH:CH.CHO$, melting at 51°; with acetone, **Furfur-acetone**, $C_4H_3O.CH:CH.CO.CH_3$; with acetophenone, **furfural-mono- and diacetophenone**, and **Difurfural Triacetophenone** (B. 29, 2248). (3) Just as potassium cyanide in alcoholic solution changes benzaldeyde to benzoïn, so it converts furfurol into **furoïn**, $C_{10}H_8O_4$, melting at 135°: $2C_4H_3O.CHO = C_4H_3O.CH(OH).CO.C_4H_3O$. This is in every way similar to benzoin. Furoïn is oxidized in alkaline solution by the oxygen of the air to **Furil**, $C_4H_3O.CO.CO.C_4H_3O$. This corresponds to benzil. Tin and hydrochloric acid reduce it to desoxyfuroïn, $(C_4H_3O)CH_2.CO(C_4H_3O)$ (B. 28, R. 992). **Furil digested with caustic potash becomes furilic acid**, $(C_4H_3O)_2C(OH)COOH$,

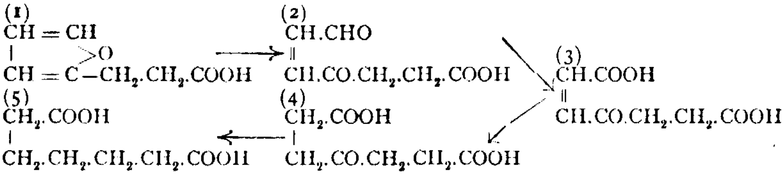
analogous to benzilic acid. Compare B. **25**, 2843, for the condensation products of furoïn with o-diamines.

(4) Furfurane **acids**, with unsaturated side-chains, are produced, in the condensation of furfurol and fatty acids, on heating it with the anhydrides and sodium salts of the fatty acids. This is analogous to the formation of cinnamic acid from benzaldehyde. Furfur-acrylic acid results on heating furfurane with acetic anhydride and sodium acetate:

$$C_4H_3O.CHO + CH_3.CO_2Na = C_4H_3O.CH:CH.CO_2Na + H_2O.$$

Furfur-acrylic Acid, $C_7H_6O_3$, melting at 141°, is also formed from *furfur-malonic acid*, the condensation product of furfurol and malonic ester (B. **24**, 143; **27**, 283). Furfur-acrylic acid, like cinnamic acid, occurs in an *allotropic modification* (B. **28**, 129). The acid, when heated with hydrochloric acid, has its ring decomposed, and acetone diacetic acid results. Sodium amalgam converts it into

Furfur-propionic Acid (1), $C_4H_3O.CH_2.CH_2.CO_2H$, melting at 51°. Bromine-water disrupts the furfurane ring in this compound, and the product is *furon-aldehyde* (2), which can be gradually converted step by step into furonic acid (3), hydrofuronic acid (4), or acetone diacetic acid and pimelic acid (5):



This conversion of furfurol into n-pimelic acid proves that the aldehyde group is in the α-position.

Furfur-angelic Acid, $C_4H_3O.CH:C(CH_2.CH_3).COOH$, from furfurol and butyric acid, melts at 88°, and passes into the corresponding **Furfur-valeric Acid** under the influence of sodium amalgam.

Furfurol condenses with lævulinic acid, depending upon whether alkaline or acid solvents are employed, either to δ- or β-**Furfurol-lævulinic acid**, $C_4H_3O.CH:CH.-CO.CH_2.CH_2.COOH$, or $C_4H_3O.CH:C(CO.CH_3).CH_2COOH$. The latter changes readily with *benzene ring-formation* into aceto-oxycumarone (p. 462).

(5) **Furfuramide**, $(C_5H_4O)_3N_2$, melting at 117°, results from the action of aqueous ammonia upon furfurol (same as hydrobenzamide from benzaldehyde, see this).

Boiling water decomposes it into furfurol and ammonia. If boiled with KOH it undergoes a transposition into the isomeric base, **Furfurin**, melting at 116° (compare glyoxalines).

α-**Methyl Furfurol**, $C_4H_2(CH_3)O.CHO$, boiling at 184-186°, occurs together with furfurol in wood oil (B. **22**, 608). It is also present in the product obtained by distilling varec with sulphuric acid. When rhamnose (1, 530) is distilled with sulphuric acid, it results, just as furfurol is obtained from arabinose (B. **22**, R. 752).

Carboxylic Acids of Furfurane: α-**Furfurane-carboxylic Acid** (compare C. 1897, II, 268), $C_4H_3O.CO_2H$, *pyromucic acid*, melting at 134° with sublimation, is obtained by the oxidation of furfurol, and in the distillation of mucic and isosaccharic acids (p. 447); it, therefore, contains the carboxyl group in the α-position.

History.—Scheele, in 1780, observed pyromucic acid as a product of the distillation of mucic acid. Pelouze (1834) determined its composition and v. Baeyer established its constitutional formula.

Its *ethyl ester*, $C_4H_3O.CO_2.C_2H_5$, melts at 34° and boils at 210° C. Its *chloride*, $C_4H_3O.COCl$, boils at 170°. Ammonia converts this into an *amide*, $C_4H_3O.CO.NH_2$,

which is changed into *furfuryl-nitrile*, $C_4H_3O.CN$, by PCl_3. The nitrile can also be obtained from furfuraldoxime by the exit of water. See C. 1897, 1, 1024, for the *hydrazide*, *azide*, etc.

Bromine vapor converts pyromucic acid into a *tetrabromide*, $C_4H_3OBr_4.CO_2H$, which is oxidized to dibromsuccinic acid by chromic acid. Fumaric acid results on evaporating pyromucic acid with bromine water. An excess of bromine or chlorine water produces mucobromic acid and mucochloric acid (1, 365).

a-**Brom-pyromucic Acid**, $C_4H_2BrO.CO_2H$, is formed by heating the tetrabromide, and by brominating pyromucic acid in glacial acetic acid solution. It melts at 184° (B. **19**, R. 241). *β*-**Brompyromucic Acid**, from the two dibrompyromucic acids and zinc, melts at 129° (B. 17, 1759).

Nitropyromucic Acid, $C_4H_2(NO_2)O.CO_2H$, melting at 183°, is formed by nitrating furfurane dicarboxylic acid and by oxidizing nitroethylene-nitrofurfurane (B. **18**, 1362).

a,a_1-**Furfurane Dicarboxylic Acid**, $C_4H_2O(CO_2H)_2$, *dehydromucic acid*, is produced by heating mucic acid to 100° with hydrochloric acid. It dissolves with difficulty in water, and when heated breaks down into carbon dioxide and pyromucic acid.

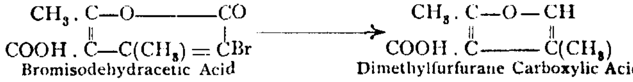
Homologous furfurane-carboxylic acids can be obtained synthetically from *γ*-diketone carboxylic esters by the exit of water.

Methylpyromucic Acid, $C_4H_2(CH_3)O.COOH$, melting at 109°, obtained from methyl furfurol (B. **22**, 608), is decomposed by bromine water into acetoacrylic acid (1, 382) (B. **23**, 452).

a,a_1-**Dimethyl Furfurane-*β*-carboxylic Acid, Pyrotritartaric Acid**, $C_4H(CH_3)_2$-$O.CO_2H$ (B. **20**, 1074), **Uvinic Acid**, melting at 135° C., may be obtained (1) from acetonyl acetoacetic ester; (2) from carbopyrotritartaric acid and from methronic acid by the splitting-off of carbon dioxide; (3) from tartaric acid by distillation; (4) from pyroracemic acid by protracted boiling with baryta-water or sodium acetate, etc.

When heated to 150–160° with steam it breaks up into carbon dioxide and acetonyl acetone. Rapidly distilled, it decomposes into carbon dioxide and dimethyl furfurane.

a,β_1-**Dimethylfurfurane-*β*-carboxylic Acid**, melting at 122°, is isomeric with pyrotritartaric acid. It is formed from bromisodehydracetic acid (B. **26**, 755):



Bromisodehydracetic Acid — Dimethylfurfurane Carboxylic Acid.

(Compare the formation of coumarones from coumarine dibromides, p. 462.)

a,a_1-**Methylphenylfurfurane-*β*-carboxylic Acid**, $C_4H\left(\begin{matrix}CH_3\\C_6H_5\end{matrix}\right)O.CO_2H$, from acetophenon-acetoacetic ester, melts at 181°, and when heated breaks down into CO_2 and methylphenyl-furfurane (B. 17, 2764).

a,a_1-**Dimethylfurfurane-β,β_1-dicarboxylic Acid**, $C_4(CH_3)_2O(CO_2H)_2$, **carbopyrotritartaric acid**, melting at 261°, results upon boiling diacetsuccinic ester with dilute sulphuric acid (Knorr, B. **17**, 2864; **22**, 146). Consult B. **27**, 1158, upon *isocarbopyrotritartaric acid*. Carbopyrotritartaric acid at higher temperatures breaks up into carbon dioxide and pyrotritartaric acid.

Methronic Acid, $C_8H_8O_5$, is isomeric with carbopyrotritartaric acid. It is produced by digesting acetoacetic ester with sodium succinate and acetic anhydride (B. **18**, 3410). By similar action acetoacetic ester and pyrotartaric acid yield methyl methronic acid. Methronic acid melts at 204°.

It is also produced, together with sylvan-acetic acid, poorer in CO_2 (B **21**, R. 636), by the condensation of acetoacetic ester with glyoxal. Because of this method of formation, and also by virtue of its passage to pyrotritartaric acid, methronic acid has been ascribed the formula of a *methyl-furfurane-acetic carboxylic acid*, $C_4HO(CH_3)(CH_2.COOH)COOH$ (B. **22**, 152). Compare A. **250**, 166, for another view of its constitution.

Hydrofurfuranes: But few hydrofurfurane derivatives have been obtained by the reduction of furfuranes—*e. g.*, *tetrahydro-a,a_1-methyl-phenyl-furfurane*, $C_4H_6(CH_3)(C_6H_5)O$, boiling at 230°, from methyl-phenyl furfurane (p. 449), *tetrahydrodiphenyl furfurane* (B. **23**, R. 744), etc.

Dihydrofurfurane, C_4H_6O, boiling at 67°, may be prepared synthetically by reducing erythrol. PCl_5 converts it into furfurane (Bull. soc. chim. **35**, 418).

a-**Methyldihydrofurfurane**, $C_4H_5(CH_3)O$, is obtained from acetopropyl alcohol (I, 318, and B. **22**, 1196). Additional **dihydrofurfurane compounds** have been prepared synthetically from *a*-chlorcrotonic ester and chlorfumaric ester by condensation with sodacetoacetic ester and sodium benzoyl acetic ester (B. **29**, R. 859).

Tetramethylene oxide, $\begin{matrix} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{matrix}\!\!>\!O$, and its homologues (I, 299) are tetrahydrofurfuranes; the *γ*-lactones—*e. g.*, butyrolactone, $\begin{matrix} CH_2-CO \\ | \\ CH_2-CH_2 \end{matrix}\!\!>\!O$ (I, 345)—and the anhydrides of the succinic acid series—*e. g.*, $\begin{matrix} CH_2-CO \\ | \\ CH_2-CO \end{matrix}\!\!>\!O$ (I, 447), etc.—are keto- and diketotetrahydrofurfuranes. Tetronic acid, $\begin{matrix} CO-CH_2 \\ | \\ CH_2-CO \end{matrix}\!\!>\!O$ (I, 482), and its homologues are metameric with the latter.

2. THIOPHENE GROUP.*

Thiophene, C_4H_4S, an analogue in constitution of furfurane, C_4H_4O, exhibits the greatest similarity to benzene. It may be viewed as benzene, in which one of the three acetylene groups, CH : CH, has been replaced by S. By the replacement of the 4-H atoms in thiophene by other elements or groups we obtain innumerable derivatives, in all respects analogous to those derived from benzene. *All* thiophene compounds give an intense blue coloration—the indophenin reaction, B. **16**, 1473—when mixed with a little isatin and concentrated sulphuric acid.

History.—Thiophene, as well as the methylated thiophenes, are invariably associated with the benzene hydrocarbons which are prepared technically from coal-tar. Therefore, before thiophene was discovered, the indophenin reaction was considered as characteristic of benzene hydrocarbons. V. Meyer (1883) observed an absence of this reaction when working with a benzene preparation made from benzoic acid, and that it reappeared when commercial benzene containing sulphur was employed in the test. This led to the discovery of thiophene. The same investigator ascertained the constitution of the latter and its kinship to furfurane and pyrrol. Thionessal, discovered by Laurent in 1841, is a thiophene derivative, but it was only in 1891 that Baumann and Fromm proved it to be tetraphenylthiophene.

The *synthetic methods* of producing thiophene compounds from *γ*-dicarbonyl derivatives have been discussed (I, 318; II, 447). The more special procedures are the ready conversion of *γ*-ketone acids into oxythiophenes by means of P_2S_5, and thiophenes result when the primary oxythiophenes are reduced with P_2S_3 (B. **19**, 551; **23**, 1495):

$$\begin{matrix} CH_2-CO-CH_3 \\ | \\ CH_2-COOH \end{matrix} \longrightarrow \begin{matrix} CH=C.CH_3 \\ | \\ CH=C.OH \end{matrix}\!\!>\!O \longrightarrow \begin{matrix} CH=C.CH_3 \\ | \\ CH=CH \end{matrix}\!\!>\!S$$

Lævulinic Acid — 1,4-Oxythiotolene — 1- or *a*-Thiotolene.

Thiophene, C_4H_4S, boiling at 84°, with sp. gr. 1.062 (23°), occurs in coal-tar (B. **28**, 492), just as do the methyl thiophenes; indeed, the individual thiophenes are present (to upward of 0.6 per cent.) in the corresponding commercial benzene hydrocarbons, as they have the same

* V. Meyer, "Die Thiophengruppe," 1888.

boiling points. Thiophene is found in benzene, methyl thiophenes in toluene, etc. Thiophene is also formed in considerable abundance by heating a mixture of sodium succinate and phosphorus trisulphide (Volhard and Erdmann, B. **18**, 454):

$$\begin{array}{l} CH_2—COONa \\ \mid \\ CH_2—COONa \end{array} \longrightarrow \begin{array}{l} CH = CH \diagdown \\ \mid \qquad\qquad\quad S. \\ CH = CH \diagup \end{array}$$

Thiophene also results upon heating crotonic acid, butyric acid, paraldehyde, etc., with phosphorus trisulphide: by conducting ethyl sulphide through tubes heated to redness or passing illuminating gas over heated pyrite, FeS_2, and acetylene or ethylene over boiling sulphur.

Unsaturated benzenes, when heated with sulphur, yield phenylated thiophenes. Thus, styrol forms diphenylthiophene; stilbene, tetraphenylthiophene; and acetylene dicarboxylic acid, thiophene tetracarboxylic acid (B. **28**, 1635; **30**, 110). Thiophene is obtained from crude benzene by shaking it with a little concentrated sulphuric acid (4–10 per cent.) (B. **17**, 792).

Thiophene is a colorless liquid, with an odor resembling that of benzene. It becomes crystalline when exposed to a mixture of solid carbon dioxide and ether. Sodium has no effect upon it, even when it is heated. Mixed with a little sulphuric acid and isatin it becomes dark blue in color. The same occurs when its solution in sulphuric acid is added to phenanthraquinone in glacial acetic acid (reaction of Laubenheimer, B. **19**, 673).

It is remarkable that thiophene, which from its formula cannot be regarded as a cyclic, unsaturated alkyl sulphide, does not exhibit the additive power of normal alkyl sulphides for methyl iodide, oxygen, etc. When thiophene is heated to 200° with piperidine, sulphur is eliminated and a base produced which yields *tetramethylenedipiperidine*, $C_5H_{10}N(CH_2)_4NC_5H_{10}$, upon reduction (B. **28**, 2217).

This very striking analogy existing between bodies of the *thiophene* series and the *benzene* series may be observed with the following representatives of both groups, the boiling and melting points of which compounds are presented in the table. The benzene derivatives have already been discussed; those of thiophene will receive attention in the succeeding pages:

Benzene Series.	B. P.	Thiophene Series.	B. P.
Benzene (p. 47),	80.5°	Thiophene,	84°
Toluene (p. 53),	110.3°	Thiotolene,	113°
p-Xylene (p. 54),	138°	1,4-Thioxene,	135°
Isopropyl Benzene (p. 55),	153°	Isopropyl Thiophene,	154°
Diphenyl (p. 35),	254°	Dithiënyl,	266°
Diphenyl Methane (p. 342),	261°	Dithiënyl Methane,	267°
Chlorbenzene (p. 58),	132°	α-Chlorthiophene,	130°
p-Dichlorbenzene (p. 58),	172°	Dichlorthiophene,	170°
Brombenzene (p. 59),	155°	α-Bromthiophene,	150°
Tetrabrombenzene (p. 59),	329°	Tetrabromthiophene,	326°
p-Dinitrobenzene (p. 67),	299°	Dinitrothiophene,	290°
Benzoic Acid (p. 193),	250°	α-Thiophene Carboxylic Acid,	260°
Benzonitrile (p. 202),	191°	Thiophen-nitrile,	190°
Acetophenone (p. 189),	202°	Acetothiënone,	213°
Benzophenone (p. 345),	307°	Thiënone,	326°
Cinnamic Acid (p. 274),	m. p. 133°	Thiënyl Acrylic Acid,	m. p. 138°

1. ***Thiophene Homologues.***—**Homologous thiophenes, in addition to their synthetic formation from γ-dicarbonyl compounds, are prepared from thiophene according to methods perfectly similar to those used in the production of the corresponding benzene hydrocar-**

bons from benzene; thus, from iodthiophene and an alkyl iodide by means of sodium; from thiophene, alkyl bromides and aluminium chloride, etc. The behavior of the thiophene homologues, when subjected to oxidation, etc., is analogous to that of the corresponding benzenes.

α-**Methyl Thiophene.**

α-**Thiotolene**, from iodthiophene by the aid of methyl iodide and sodium, is converted into *α*-thiophenic acid by oxidation.

β-**Methyl Thiophene**, *β*-**Thiotolene**, is formed when sodium pyrotartrate is heated with P_2S_3.

Both thiotolenes occur in coal-tar.

Dimethyl Thiophenes or **Thioxenes** occur in crude xylene (B. **29**, 2560). **1,2-Dimethyl Thiophene** boils at 136°. **1,3-Dimethyl Thiophene** boils at 138°. *1,4-Thioxene boils at 135°.* *2,3-Dimethyl Thiophene* boils at 145°. **Isopropyl Thiophene**, boiling at 154°, is formed when aluminium chloride acts upon thiophene and isopropyl bromide.

α-**Phenylthiophene**, melting at 41°, is prepared by heating benzoyl propionic acid (B. **19**, 3140).

α,*α*$_1$-**Diphenyl Thiophene**, melting at 153°, results from diphenacyl and P_2S_5 or from styrene or cinnamic acid with sulphur (B. **28**, 890), together with *α*,*β*$_1$-**diphenylthiophene**, melting at 119°. **Tetraphenyl Thiophene, Thionessal**, $C_4(C_6H_5)_4S$, melting at 184°, is produced when thiobenzaldehyde is heated; also from stilbene and sulphur (A. **38**, 320; B. **24**, 3310), just as thiophene is formed from ethylene and sulphur (see above).

Dithiënyl, $C_4H_3S.C_4H_3S$, melting at 83° and boiling at 266°, is obtained, like diphenyl, by conducting the vapors of thiophene through tubes heated to redness. An isomeric *α*,*α*$_1$-**Dithiënyl**, melting at 33°, results in the action of sulphuric acid upon thiophene and also by the interaction of *α*-iodthiophene and silver (B. **27**, 2919; **27**, 2385). **Dithiënyl Methane**, $(C_4H_3S)_2CH_2$, melting at 43° and boiling at 267°, is formed from thiophene and methylal. **Thiënyl Diphenyl Methane**, $(C_4H_3S).CH(C_6H_5)_2$, melting at 63° and boiling at 335°, is prepared from thiophene and benzhydrol. **Thiënyl Triphenyl Methane**, $(C_6H_5)_3C(C_4H_3S)$, melting at 237°, is formed when P_2O_5 acts upon triphenylcarbinol and thiophene. The homologous thiophenes may also be as readily condensed with triphenyl carbinol (B. **29**, 1402).

Dithiënyl Phenyl Methane, $C_6H_5.CH(C_4H_3S)_2$, melting at 75°, has been prepared by the condensation of benzaldehyde and thiophene (B. **29**, 2205).

2. *Halogen Derivatives:* Chlorine and bromine attack thiophene in the cold. The action is even more energetic than with the benzenes. Iodine, in the presence of mercuric oxide, also attacks it at the ordinary temperature. The three halogens first enter the *α*-position. In properties the haloid thiophenes are very similar to the benzene haloids. When the brominated thiophenes are oxidized with strongly cooled, concentrated nitric acid, the ring is ruptured and there result dibrom-maleïc acid, brom-citraconic acid, dibromacetoacrylic acid, etc.

α-**Chlorthiophene**, C_4H_3ClS, boils at 130°, and **Dichlorthiophene**, $C_4H_2Cl_2S$, at 170°. **Tetrachlorthiophene**, C_4Cl_4S, melts at 36°, and boils from 220–240°.

α-**Bromthiophene** boils at 150°. *α*,*α*$_1$-**Dibromthiophene** boils at 211°. Its formation serves for the complete isolation of all the thiophene that may be present in a thiophene-benzene (B. **18**, 1490). **Tribromthiophene** melts at 29° and boils at 260°. **Tetrabromthiophene**, C_4Br_4S, melts at 112° and boils at 326°. It is also produced in the energetic bromination of substituted thiophenes when the substituents are displaced (B. **26**, 2457).

α-**Iodthiophene**, C_4H_3IS, boils at 182°.

3. *Nitro-derivatives:* The action of nitric acid upon thiophene is so very energetic that in order to moderate the reaction, air charged with thiophene vapor is conducted into the fuming nitric acid. Mono- and dinitrothiophene are then produced (B. **17**, 2648).

Nitrothiophene, $C_4H_3(NO_2)S$, melts at 44° and boils at 225°.

Dinitrothiophene, $C_4H_2(NO_2)_2S$, melts at 52° and boils at 290°. Caustic potash colors its alcoholic solution dark red. The same coloration of dinitrobenzene, caused in the same way, is due to admixed dinitrothiophene (B. **17**, 2778).

4. *Amido-derivatives:* Nitrothiophene is reduced with much more difficulty than the nitrobenzenes. The reduction succeeds when zinc and hydrochloric acid are allowed to act upon the dilute alcoholic solution (B. **18**, 1490).

Amidothiophene, Thiophenin, $C_4H_3S.NH_2$, is a bright yellow oil. It resinifies on exposure to the air. Its HCl-salt consists of deliquescent needles. It does not yield a diazo-derivative. It combines with salts of diazobenzene, forming stable, mixed azo-dyestuffs—*e. g.*, $C_6H_5.N:N-C_4H_2S.NH_2.HCl$ (B. **18**, 2316).

5. *Sulphonic Acids:* Like the benzene sulphonic acids, the thiophene sulpho-derivatives are produced by dissolving thiophene in sulphuric acid. In this reaction the thiophene must be diluted with petroleum ether, benzene, or some other agent. They can also be prepared from the thionyl-ketones by displacing the ketone groups by sulpho-residues (B. **19**, 674, 1620, 2623; **29**, 2562).

6. *Oxythiophenes:* **Oxythiophene** is not known. α-**Oxy**-α_1-**methylthiophene, Oxythiotolene,** $C_4H_2(CH_3)S.OH$, is synthetically prepared from lævulinic acid. α-**Thiënylsulphydrate,** $C_4H_3S.SH$, is prepared by reducing α-thiophene-sulphonic chloride, $C_4H_3S.SO_2Cl$. It is present in the crude thiophene product obtained by distilling succinic acid with P_2S_5. It boils about 166°.

7. *Aldehydes and Ketones:* α-**Thiophenaldehyde,** $C_4H_3S.CHO$, results from the distillation of thiënylglyoxylic acid. It boils at 198°. See B. **24**, 47; **25**, 2588, for the thiophene aldoximes.

If oxidized, even in the air, it forms α-thiophenic acid. Aqueous caustic potash converts it into thiophenic acid and thiophene alcohol: $2C_4H_3S.CHO + KOH = C_4H_3S.CO_2K + C_4H_3S.CH_2.OH$.

α-**Thiophene Alcohol** is an aromatic liquid, boiling at 207°.

Thiophene aldehyde condenses with sodium acetate and acetic anhydride to *Thiënyl Acrylic Acid*, $C_4H_3S.CH:CH.COOH$, melting at 118°. This acid corresponds to cinnamic acid.

The ketone derivatives of thiophene are obtained very easily by the action of acid chlorides upon thiophene in the presence of aluminium chloride.

α-**Thiënyl-methyl Ketone,** $C_4H_3S.CO.CH_3$, Acetothiënone, is an oil, boiling at 213°. If it be oxidized with permanganate, it first forms **Thienyl-glyoxylic Acid,** $C_4H_3S.CO.CO_2H$, melting at 91°, and then α-thiophenic acid.

Compare B. **24**, 232, R. 627, 952, for the condensation products of acetothiënone with oxalic ester. **Dithiënyl Ketone,** *Thiënone*, $CO(C_4H_3S)_2$, melting at 88° and boiling at 326°, is obtained from thiophene and $COCl_2$. **Thiënyl Phenyl Ketone,** $C_4H_3S.CO.C_6H_5$, melting at 55° and boiling at 360°, results from thiophene, benzoyl chloride, and Al_2Cl_6.

See B. **28**, 1804, for the brominated thiophene ketones.

8. THIOPHENE CARBOXYLIC ACIDS.

Thiophene carboxylic acids are formed by methods which are perfectly analogous to those employed in the preparation of the aromatic acids:

(1) By the oxidation of the alkyl thiophenes with a solution of alkaline potassium permanganate. α-Ethyl-thiophene first yields thiënyl glyoxylic acid, but this changes to thiophenic acid.

(2) By the action of chlor-carbonic ester and sodium amalgam upon iod- or brom-thiophenes, or by the interaction of the same reagent and thiophene, or the latter, urea chloride, and Al_2Cl_6.

α-**Thiophene Carboxylic Acid,** $C_4H_3S.CO_2H$, melting at 126° and boiling at 260°, is also formed upon heating mucic acid with barium sulphide (p. 447).

Its *nitrile*, $C_4H_3S.CN$, is produced when α-thiophene sulphonic acid is distilled, or by the elimination of water from thiophene aldoxime (B. **25**, 1311).

β-**Thiophene Carboxylic Acid** is produced when β-methyl thiophene is oxidized. It melts at 136°.

(1,2)-**Thiophene Dicarboxylic Acid,** $C_4H_2S.(CO_2H)_2$, melts at 260° with decomposition. Like phthalic acid, it forms a *fluoresceïn* with resorcinol.

The (1,3)-*acid* melts at 118°. The (1,4)-*acid* sublimes at 300°. Sodium amalgam reduces it to—

Tetrahydro-thiophene Dicarboxylic Acid, $C_4H_6S(CO_2H)_2$, melting at 162°. This reduces ammoniacal silver solutions, especially upon warming. It resembles the hydrophthalic acids (B. **19**, 3274) in its entire deportment.

Thiophene Tetracarboxylic Methyl Ester, $C_4(COOCH_3)_4S$, melting at 127°, is obtained when acetylene dicarboxylic methyl ester is heated with sulphur to 150–155° in a sealed tube (B. **28**, 1635).

Thiophthene, $\begin{matrix} CH & — & C & — & CH \\ \| & & \| & & \| \\ CH & —S— & C & —S— & CH \end{matrix}$, consists of two thiophene nuclei, having two C-members in common. It boils at 225°. It results when citric acid is heated with P_2S_3 (B. **19**, 2444).

3. **Selenophene.**—The selenophenes are constituted analogously to the thiophenes. They contain an atom of selenium for sulphur. **Selenophene,** $\begin{matrix} CH = CH \\ | \\ CH = CH \end{matrix}\!\!>Se$, itself has not yet been prepared in a pure condition. It probably is formed when selenium ethide is conducted through tubes heated to redness (B. **18**, 1772).

α,α_1-**Dimethyl Selenophene, Selenoxene,** $C_4H_2(CH_3)_2Se$, boiling at 153–155°, is produced when acetonylacetone is heated with phosphorus selenide (B. **18**, 2255). Isatin and sulphuric acid color it a carmine-red. It also shows the *Laubenheimer reaction* (p. 453).

4. PYRROL GROUP.*

In pyrrol, C_4H_5N, there is a four-membered carbon chain united to a ring by the bivalent imide group. It is, therefore, a secondary amine, and, like its derivatives, possesses a feeble basic nature, as it dissolves in dilute acids. The pyrrol bodies, on the other hand, show great similarity in their behavior to the phenols; the imide hydrogen can be easily replaced by potassium. The great reactivity of the methine hydrogen in pyrrol is quite remarkable. It can be as readily, and in some instances more easily, replaced than the imide hydrogen by the most different groups and atoms. The constitution of pyrrol and its relations to furfurane and thiophene are deduced from its analogous syntheses from the γ-dicarbonyl compounds.

A rather remarkable occurrence is the reversal of these syntheses—*i. e.*, the decomposition of the pyrrol ring with elimination of the imide group. This is induced by the action of hydroxylamine. Dioximes are thus produced. Thus, pyrrol yields succindialdoxime (B. **22**, 1968):

$$\begin{matrix} CH = CH \\ | \\ CH = CH \end{matrix}\!\!>NH + 2H_2N.OH = \begin{matrix} CH_2.CH:N.OH \\ | \\ CH_2.CH:N.OH \end{matrix} + NH_3.$$

The homologous pyrrols—*e. g.*, α-methyl pyrrol, β-isopropyl, etc.—react similarly. This decomposition can be applied in determining the position of the substituents in the homologous pyrrols, as the α-alkyl pyrrols yield the oximes of ketones, while aldoximes are obtained from the β-substituents. These can be readily converted into dibasic acids (B. **24**, R. 649, 830).

The positions of substituents in the methine groups of pyrrols are indicated, as with furfurane and thiophene, by means of numbers, 1, 2, 3, 4, etc., or letters, α, α_1, β, β_1, etc. (compare 448).

The derivatives obtained by replacement of the imide hydrogen atom are termed *n*- (or *N*-) *derivatives* to distinguish them from the C-compounds.

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* Ciamician, "Il Pirrolo ed i suoi derivati," Roma, 1888.

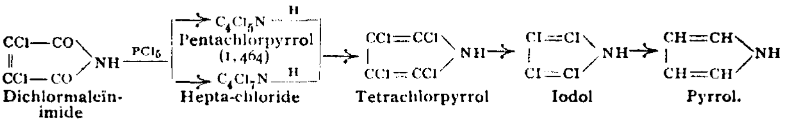
Pyrrol, boiling at 131°, with sp. gr. 0.9752 (12.5°), received its name from its property of imparting a fiery red (πυῤῥός) color to a pine shaving moistened with hydrochloric acid. It was first found in coal-tar and bone oil (Runge, 1834; Anderson, 1858). It also is present in the distillation products of bituminous shales.

Bone oil, freed from the strongly basic substances (chiefly pyridine bases), consists of nitriles of the fatty acids, which are saponified upon boiling them with caustic potash, and in addition benzene hydrocarbons, pyrrol and its homologues. The pyrrol is contained in that portion of the oil boiling at 115–130°, which is treated with metallic potassium, whereupon solid potassium-pyrrol separates.

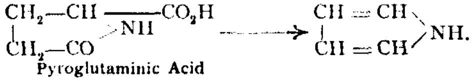
The oil obtained free from bone-glue by distillation is composed almost entirely of pyrrol compounds.

Pyrrol can be obtained synthetically (1) by the distillation of ammonium saccharate or mucate, or upon heating glycerol to 200°; (2) when acetylene and ammonia are conducted through tubes heated to redness: $2C_2H_2 + NH_3 = C_4H_4NH + H_2$; (3) from various acid imides and lactams, which may also be regarded as keto-derivatives of pyrrol hydrides. Thus, succinimide is reduced to pyrrol when it is distilled with zinc-dust (or sodium):

Succinimide and dichlormaleïnimide, when heated with PCl_5, yield perchlorinated products, which, upon reduction, become tetrachlorpyrrol. The latter can be changed through tetraiodpyrrol into pyrrol:

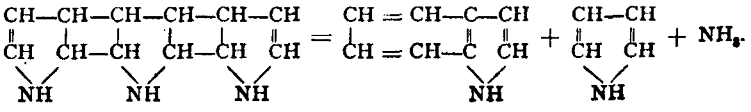


Pyrrol is also produced when pyroglutaminic acid (1, 493) is heated:



Pyrrol is a colorless liquid with an odor resembling that of chloroform. It becomes brown on exposure to the air. It is but slightly soluble in water, but dissolves very readily in alcohol and ether. In yields an indigo blue coloration with isatin and sulphuric acid, or with phenanthraquinone, etc. (p. 447) (B. **17**, 142, 1034; **19**, 106). Pyrrol is a very feeble base. It is dissolved very slowly in the cold by dilute acids, but is rapidly resinified by strong acids. When its solutions in dilute acids are heated, ammonia is disengaged and an amorphous red powder of varying composition is precipitated. This is *pyrrol red*.

The resinifying action of acids upon pyrrols is probably due to polymerization changes (B. **26**, 1711). Thus, dry hydrochloric acid gas precipitates $(C_4H_5N)_3HCl$ from the ethereal solution of pyrrol. This must be regarded as the salt of a polymeric tripyrrol, $(C_4H_5N)_3$. Crystalline tripyrrol is obtained by neutralizing the solution of pyrrol in dilute aqueous hydrochloric acid with ammonia and then extracting with ether. Tripyrrol polymerizes further on standing, but when heated it breaks down into NH_3, indol, and pyrrol, according to the following equation (B. **27**, 476):



Compare the analogous decomposition of polymeric alkyl pyrrols into alkylic indols (p. 459).

The transition of the pyrrol ring to that of pyridine is very remarkable.

β-Chlorpyridine is formed upon heating potassium-pyrrol, or pyrrol and sodium alcoholate, with chloroform:

$$\begin{matrix} CH = CH \\ | \\ CH = CH \end{matrix}\!\!>NK + CHCl_3 = \begin{matrix} CH = CCl.CH \\ | \qquad\qquad \| \\ CH = CH{-}N \end{matrix} + KCl + HCl.$$

Brom-pyridine.

Similarly, bromoform yields β-brompyridine, and methylene chloride, pyridine, etc. The homologous alkyl pyrrols, when heated alone to higher temperatures, also form pyridine derivatives.

N-Derivatives of Pyrrol: Potassium dissolves in pyrrol with an energetic evolution of hydrogen. It forms **Potassium-pyrrol**, $C_4H_4NK = \begin{matrix} CH - CH \\ | \\ CH = CH \end{matrix}\!\!>NK$, a crystalline mass. This compound may also be obtained by boiling pyrrol with solid caustic potash. Water regenerates pyrrol and caustic potash. Sodium does not act like potassium.

A series of N-derivatives of pyrrol may be prepared from potassium pyrrol. They are characterized by the fact that they change, on heating, to C-derivatives. This is analogous to the formation of homologous anilines from the alkylic anilines:

Alkyl iodides yield **n-Alkyl Pyrrols**, $C_4H_4:NR$, which can be directly formed if in the pyrrol syntheses primary amines be substituted for ammonia, and also in the distillation of the alkylamine salts of mucic acid, etc.

n-**Methyl Pyrrol** boils at 113°. n-**Ethyl Pyrrol** boils at 131°. n-**Isoamyl Pyrrol** boils at 180–184°.

n-**Phenyl Pyrrol**, from aniline mucate, melts at 62°.

n,β-**Pyridyl Pyrrol**, $C_4H_4N.C_5H_4N$, boiling at 251°, is obtained from β-amidopyridine mucate (B. **28**, 1907).

With acetyl chloride the product is: n-**Acetyl Pyrrol**, $C_4H_4N.CO.CH_3$, boiling at 178°. It is also produced (together with pyrrol-methyl-ketone) upon heating pyrrol with acetic anhydride.

Phosgene converts potassium-pyrrol into n-**Carbonyl Pyrrol**, $CO<\begin{matrix} N.C_4H_4 \\ N.C_4H_4 \end{matrix}$, melting at 63° and distilling at 238°. When heated, it is converted into isomeric dipyrryl ketone, $CO<\begin{matrix} C_4H_3.NH \\ C_4H_3.NH \end{matrix}$.

n-**Pyrrol Carboxylic Ester**, $C_4H_4N.CO_2.C_2H_5$, is formed when chlor-carbonic ester acts upon potassium-pyrrol. It is an oil boiling at 180°. It passes into **Pyrrol Carbamide**, $C_4H_4N.CO.NH_2$, if it is heated with aqueous ammonia.

n-**Cyan Pyrrol**, $C_4H_4N.CN$, is produced in the action of cyanogen chloride upon potassium-pyrrol. It rapidly polymerizes to a melamine derivative.

n-*Anilido*-derivatives of the pyrrols, $C_4R_4N.NHC_6H_5$, have been synthetically obtained from 1,4-diketo compounds and phenylhydrazine (compare A. **289**, 312).

C-Derivatives of Pyrrol: 1. C-**Alkyl Pyrrols**, *homologous pyrrols*, occur in bone oil. They are artificially produced:

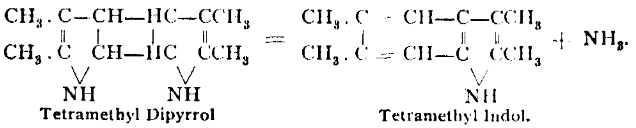
(a) On conducting the vapors of pyrrol and alcohols over zinc-dust;

(b) Upon heating pyrrol or potassium-pyrrol with alkyl iodides. n-Alkyl pyrrols result at first, but they immediately change to c-alkyl pyrrols;

(c) By splitting off carbon dioxide from the homologous pyrrol carboxylic acids (p. 460);

(d) By direct synthesis from γ-diketones—*e. g.*, acetonyl acetone, etc.—upon heating with ammonia.

Behavior: The C-alkyl pyrrols yield the corresponding pyrrol carboxylic acids when they are fused with caustic potash. Like pyrrol itself they are readily resinified by acids. Gaseous hydrogen chloride precipitates compounds like $[C_4H_3(CH_3)NH]_2HCl$, $[C_4H_2(CH_3)_2NH]_2HCl$, from the ethereal solutions of the mono- and α,β-dialkyl pyrrols. In aqueous solution dilute sulphuric acid changes these salts, with the elimination of ammonia, into alkyl indols. The reaction completes itself by the assumption of a structure for polymeric alkyl pyrrols similar to that attributed to tripyrrol (B. **24**, 2562; **26**, 1711):



Tetramethyl Dipyrrol Tetramethyl Indol.

α-**Methyl Pyrrol** boils at 148°, while the β-variety boils at 143°.

α,β-**Dimethyl Pyrrol** boils at 165°. These three have been obtained from bone oil. α,α_1-**Dimethyl Pyrrol**, boiling at 165°, and α,β_1-**Dimethyl Pyrrol**, boiling at 160°, have been prepared from their dicarboxylic acids (p. 461).

α-**Ethyl Pyrrol**, boiling at 165°, and α-**Isopropyl Pyrrol**, boiling at 175°, are produced in the action of aldehyde or acetone and zinc chloride upon pyrrol. See B. **30**, 434, for α,α_1-**methyl isopropyl pyrrol.** α-**Phenyl Pyrrol**, melting at 129° and boiling at 272°, is formed by the rearrangement of n-phenyl pyrrol upon the application of heat (B. **28**, 1905).

α,α_1-**Methyl Phenyl Pyrrol** melts at 101°.

Tetraphenyl Pyrrol, from bidesyl with ammonia, melts at 211° (B. **22**, 553).

α,β-**Pyridyl Pyrrol**, melting at 72°, is formed by the rearrangement of n,β-pyridyl pyrrol. The methyl iodide of its n-methyl ether appears to be identical with nicotyrin iodmethylate obtained from nicotine (see this) (B. **28**, 1912).

2. *Halogen Substitution Products:* The halogens react very energetically with the pyrrol compounds. To prevent the formation of tar it is necessary to operate with very dilute solutions. Even then, as a rule, all the available hydrogen atoms of the pyrrol nucleus will be immediately replaced. Chlorine and bromine oxidize pyrrol in alkaline solution at once and convert it into dichlor or dibrom maleïnimides (p. 447).

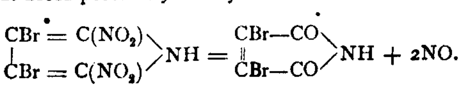
Tetrachlorpyrrol, C_4Cl_4NH, melting with decomposition at 110°, is also obtained by the reduction of the product resulting from the action of PCl_5 upon succinimide and dichlormaleïnimide—the so-called pyrrol pentachloride, C_4Cl_5N, and the heptachloride, C_4Cl_7N (1, 463). It decomposes very rapidly *spontaneously*, and cannot be directly converted into pyrrol by retrogressive substitution. Potassium iodide converts it into iodol (B. **19**, 3027).

Iodol, Tetra-iod-pyrrol, C_4I_4NH, melting at 104° with decomposition, crystallizes in yellowish-brown needles. It is best made by the action of iodine upon pyrrol in the presence of alkalies. It is odorless. It is applied as an antiseptic, having the same action as iodoform (B. **20**, R. 220).

Tetrachlor-n-phenyl-pyrrol, $C_4Cl_4 . NC_6H_5$, results when PCl_5 acts upon succinanil (1, 449).

3. *Nitro-derivatives:* Nitric acid converts pyrrol and alkyl pyrrols into resin and then oxidizes them to oxalic acid, etc. With fuming nitric acid nitro-derivatives are only obtained from the pyrrol ketones and carboxylic acids. The side-chains are sometimes replaced.

Dinitropyrrol, $C_4H_2(NO_2)_2H_2NH$, melting at 152°, is obtained from pyrrylmethyl ketone. **Dinitrodibrompyrrol**, $C_4Br_2(NO_2)_2NH$, is formed from dibrompyrrol dicarboxylic acid. It decomposes very readily with liberation of NO into dibrommaleïnimide:



4. *Pyrrol-azo-compounds:* **Azo- and Disazo-compounds, perfectly analogous to the benzene azo-dyes, result from the interaction of benzene diazo-salts and pyrrol or homol-**

ogous pyrrols. One and two molecules of the diazo-bodies enter the reaction (B. 19, 2251) (p. 113):

$$\underset{\text{Pyrrolazobenzene}}{(C_4H_3NH)N:NC_6H_5} \quad \text{and} \quad \underset{\text{Pyrroldisazobenzene.}}{(C_4H_2NH)\!<\!\begin{matrix} N:N.C_6H_5 \\ N:N.C_6H_5 \end{matrix}}$$

5. *Pyrrol Ketones:* These (together with the isomeric n-acetyl pyrrols) are produced by heating the pyrrols with acetic anhydride, and are also prepared by a *molecular* rearrangement of the n-acetyl pyrrols on being heated.

Potassium permanganate oxidizes the C-acetyl pyrrols to pyrrol-glyoxylic acids, which molten caustic potash converts into pyrrol carboxylic acids. They condense with benzaldehyde to *cinnamyl-pyrrols—e. g.*, $C_4H_3NH.CO.CH:CHC_6H_5$. The latter serve to characterize the alkyl pyrrols.

α-**Pyrryl-methyl Ketone**, $C_4H_3(CO.CH_3)NH$, melts at 90° and boils about 220°. Its **oxime** melts at 146°. Potassium permanganate oxidizes it to **pyrryl glyoxylic acid**, $C_4H_3(NH).CO.CO_2H$, melting at 75° with decomposition.

Pyrryl-dimethyl-diketone, $C_4H_2(CO.CH_3)_2NH$, melts at 162°. Potassium permanganate oxidizes it to **carbopyrrol gloxylic acid**, $C_4H_2NH(COOH)CO.COOH$.

Dipyrryl Ketone, $CO(C_4H_3.NH)_2$, melting at 100°, is formed, together with **Pyrroyl-pyrrol**, $C_4H_4N.CO.C_4H_3NH$, melting at 63°, upon heating n-carbonyl pyrrol (p. 459).

6. *Pyrrol Carboxylic Acids:* These resemble the phenol carboxylic acids, and are produced by perfectly similar methods:

(1) By the oxidation of the homologous pyrrols when fused with caustic potash.

(2) By the action of carbon dioxide upon the potassium derivatives of the pyrrols:

$$C_4H_4NK + CO_2 = C_4H_3(NH).CO_2K.$$

(3) By the action of carbon tetrachloride and alcoholic potash upon pyrrol.

(4) The esters of the homologous pyrrol carboxylic acids may be synthesized by the action of alcoholic ammonia upon γ-diketocarboxylic and dicarboxylic esters. The ammonia can be replaced by primary amines, amido-acids, hydroxylamines, phenylhydrazine ($R = H, CH_3, OH, NHC_6H_5, CH_2COOH$, etc.):

$$\begin{array}{l} CO_2.C_2H_5CH-COCH_3 \\ \qquad\quad | \\ CO_2.C_2H_5CH-CO.CH_3 \end{array} \xrightarrow{NH_2R} \begin{array}{l} CO_2C_2H_5C = C\text{———}CH_3 \\ \qquad\quad | \qquad\quad >NR \\ CO_2C_2H_5C = C\text{———}CH_3 \end{array}$$

(5) By the reduction of a mixture of isonitrosoacetoacetic ester with acetoacetic ester (similar reactions: B. 26, R. 597; 27, R. 586):

$$\underset{\substack{\text{Isonitrosoaceto-} \\ \text{acetic Ester}}}{\begin{array}{l} CH_3.CO \\ \qquad | \\ CO_2R.C = NOH \end{array}} + \underset{\substack{\text{Acetoacetic} \\ \text{Ester}}}{\begin{array}{l} CH_2.CO_2R \\ | \\ CO.CH_3 \end{array}} \longrightarrow \underset{\substack{\alpha,\beta\text{-Dimethyl-}\beta,\alpha_1\text{-pyrroldicarboxylic} \\ \text{Ester.}}}{\begin{array}{l} CH_3.C\text{————}CCO_2R \\ \qquad \| \qquad\qquad \| \\ CO_2RC-NH-CCH_3 \end{array}}$$

The pyrrol carboxylic acids readily part with carbon dioxide upon the application of heat and yield the corresponding pyrrols.

α-**Pyrrol Carboxylic Acid**, $C_4H_3NH.COOH$, melting with decomposition at 192°, is obtained in the form of its *amide*, melting at 176°, together with pyrrol when ammonium mucate is heated. A cyclic double acid amide of *α*-pyrrol carboxylic acid is **Pyrocoll**, $CO\!<\!\begin{matrix} NC_4H_3 \\ C_4H_3N \end{matrix}\!>\!CO$, melting at 268°. It is produced in the distillation of gela-

tine (κόλλα) and is artificially prepared by heating carbopyrrolic acid with acetic anhydride. When it is heated with PCl_5, *perchlorpyrocoll*, $C_{10}Cl_6N_2O_2$, is produced. The latter absorbs eight additional chlorine atoms and passes into the chloride $(C_4Cl_7NCO)_2$, which becomes tetrachlorpyrrol upon reduction (p. 459).

β-Pyrrol Carboxylic Acid, melting at 162°, is obtained by fusing methyl pyrrol with caustic potash.

Methyl Pyrrol Carboxylic Acids, $C_4H_2(CH_3)NH.COOH$. The α-acid melts at 169°; the β-acid at 142°. **α,α₁-Dimethyl-pyrrol-β-carboxylic Acid,** $C_4H(CH_3)_2.NH.COOH$, melts at 118°. Its ester is derived from the corresponding dicarboxylic esters by the exit of carbon dioxide.

α,α₁-Diphenylpyrrol Carboxylic Acid, $C_4H(C_6H_5)_2NH.COOH$, melting at 261°, is obtained from phenacylbenzoylacetic ester, $C_6H_5.CO.CH(CO_2R)CH_2.CO.C_6H_5$ (p. 381). **α,α₁-Pyrrol Dicarboxylic Acid,** $C_4H_2NH(COOH)_2$, *from* carbopyrrol glyoxylic acid (p. 461), decomposes at 200° into carbon dioxide and pyrrol. **α,α₁-Dimethyl-β,β₁-pyrrol Dicarboxylic Acid,** $C_4(CH_3)_2NH(COOH)_2$, from diacetosuccinic ester, breaks down at 251° into $2CO_2$ and α,α₁-dimethyl pyrrol. **α,β₁ Dimethyl-β,α₁-pyrrol Dicarboxylic Acid,** from acetoacetic ester with isonitrosoacetoacetic ester, decomposes at 197° into $2CO_2$ and α,β₁-dimethyl pyrrol. **αα₁-Diphenyl-β,β₁-pyrrol Dicarboxylic Ester,** melting at 152°, is produced when ammonia acts upon dibenzoyl succinic ester (A. 293, 107).

Pyrrolen-phthalide, $CO<^{C_6H_4}_{O}>C<^{C_4H_3N}_{NC_4H_3}>C<^{C_6H_4}_{O}>CO$, is produced when phthalic anhydride and pyrrol are heated together (B. 19, 2201). Its formula is probably analogous to that of pyrocoll.

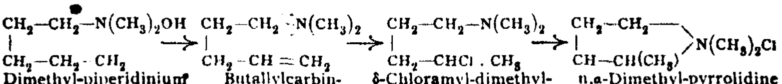
Hydropyrrol Derivatives: When pyrrol is reduced (zinc-dust and acetic acid) two hydrogen atoms are added and dihydropyrrol or pyrrolin, C_4H_7N (1, 314), is produced. Further addition of hydrogen (by means of HI and phosphorus) leads to tetrahydropyrrol or pyrrolidine, C_4H_9N. The nature of pyrrol is very essentially altered by this addition of hydrogen. Whereas pyrrol is a very feeble base, pyrroline and pyrrolidine, to even a greater degree, manifest the strong basic properties of the secondary amines of the aliphatic series.

Pyrroline, $\begin{matrix}CH = CH\\ | \\ CH_2 - CH_2\end{matrix}>NH$, is a liquid that dissolves readily in water and boils at 91°. It has an alkaline reaction, smells like ammonia, and unites with acids to form salts. It is a secondary base. Nitrous acid converts it into *nitrosamine*, $C_4H_6N(NO)$, melting at 38°.

Pyrroline and methyl iodide unite to dimethyl-ammonium iodide, $C_4H_6N(CH_3)_2I$.

n-Methyl Pyrroline, $C_4H_6N.CH_3$, is formed by the reduction of methyl pyrrol. It boils at 80°.

Pyrrolidine, Tetramethylene-imine, $\begin{matrix}CH_2 - CH_2\\ | \\ CH_2 - CH_2\end{matrix}>NH$, as well as its homologues, have already been described in connection with the aliphatic bodies. In addition to the methods there given for its production another may be introduced at this point. It represents a transition of the six-membered piperidine ring into the five-membered pyrrolidine ring. Piperidine or pentamethylene-imine combines with alkyl iodides, forming dimethylpiperidinium iodide, the hydroxide of which, upon distillation, changes to a compound with an open chain, *butallylcarbindimethylamine*. The hydrochloride addition product of the latter readily rearranges itself into the chlormethylate of n,α-dimethylpyrrolidine:



Dimethyl-piperidinium Hydroxide — Butallylcarbin-dimethylamine — δ-Chloramyl-dimethyl-amine — n,α-Dimethyl-pyrrolidine Methyl Chloride.

Other unsaturated amines analogous in constitution to butallylcarbindimethylamine can be changed by HCl to pyrrolidine bases (Merling, A. 264, 310; 278, 1). Pyrrolidine can be carried through changes similar to those indicated above for piperidine. It

may be combined with methyl iodide. The resulting dimethylpyrrolidylium iodide can then be decomposed by distillation with caustic potash, and the base dimethyl pyrrolidine, $C_4H_7N(CH_3)_2$, will be obtained. When its iodmethylate is distilled with potash the products are trimethylamine and an unsaturated hydrocarbon, **Pyrrolylene**, C_4H_6 (B. 19, 569).

n-**Methyl Pyrrolidine**, $C_4H_8N \cdot CH_3$, boiling at 81–83°, is identical with the base, which is produced by the elimination of carbon dioxide from *hygric acid* or n-*methyl-pyrrolidine carboxylic acid*, an oxidation product of the alkaloid hygrine present in coca leaves (B. 30, 1113). a,2-**Pyridyl-n-methyl Pyrrolidine** is very probably the alkaloid *nicotine*. Consult B. 30, 1588, for the reduction products of a,a_1-dimethyl pyrrol.

Ketopyrrolidines or *Pyrrolidones* are the lactams of the γ-amido-acids, like **Butyro-lactam, Pyrrolidone**, $\begin{matrix} CH_2-CO \\ | \\ CH_2-CH_2 \end{matrix}\!\!>NH$, which have also been discovered in connection with the aliphatic bodies.

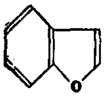
Diketopyrrolidines are the imides of the succinic acid series—*e. g.*, **succinimide**, $\begin{matrix} CH_2-CO \\ | \\ CH_2-CO \end{matrix}\!\!>NH$ (1, 448). a,β-Diketopyrrolidines are produced in the condensation of oxalacetic ester with benzalanilines—*e. g.*, a,β-**diketo-n,a_1-diphenyl-β_1-pyrrolidine carboxylic ester**, $C_6H_5N\!\!<\!\begin{matrix} CO \text{———} CO \\ | \\ CH(C_6H_5)-CH(CO_2R) \end{matrix}$, melting at 171° (B. 30, 602).

Xanthoxalanil, $\begin{matrix} CO-CO \\ | \\ CH_2-CO \end{matrix}\!\!>N \cdot C_6H_5$ (B. 24, 1252), the anil of oxalacetic acid, is a triketo-pyrrolidone.

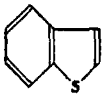
CONDENSED NUCLEI OF THE FURFURANE, THIOPHENE, AND PYRROL GROUPS.

When two adjacent C-atoms of a furfurane, thiophene, or pyrrol nucleus participate in the formation of a benzene, naphthalene, etc., group, condensed nuclei result, which sustain the same relations to the simple heterocyclic rings that the condensed nuclei of the naphthalene, phenanthrene, and anthracene groups bear to benzene.

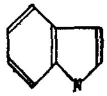
The following condensed nuclei are derived from furfurane, thiophene, and pyrrol:



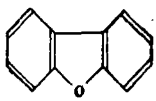
Benzofurfurane, Coumarone



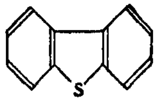
Benzothiophene



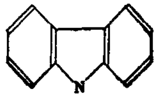
Benzopyrrol, Indol



Dibenzofurfurane, Diphenylene Oxide

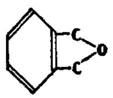


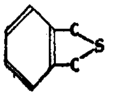
Dibenzothiophene, Diphenylene Sulphide

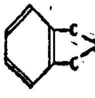


Dibenzopyrrol, Diphenylene-imide, Carbazole.

The dicyclic nuclei can have place-isomeric combinations:







These are designated isobenzofurfurane, isobenzothiophene, and isobenzopyrrol or isoïndol. These hypothetical parent substances give rise to a series of substances which have been discussed in conjunction with compounds having open chains. From isobenzofurfurane we may consider as derivatives: *tetrachlorxylylene oxide* (p. 232), *phthalide* (p. 234), *phthalic anhydride* (p. 240). To isobenzothiophene may be referred: *xylylene sulphide* (p. 232), *thiophthalide* (p. 235), *thiophthalic anhydride* (p. 240); to isoïndol: *xylyleneimine* (p. 232), *phthalimidine* (p. 234), and *phthalimide* (p. 240). To isoïndol may also be referred *methyl isoïndol*, $C_6H_4\left<\begin{matrix}CH_2 -\\ C(CH_3)\end{matrix}\right>N$, derived from phthalazine (B. 26, 710).

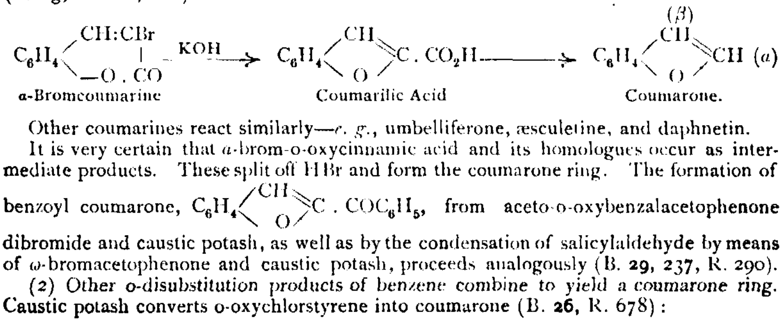
Condensed nuclei further are known in which two heterocyclic rings also participate in the formation of a benzene nucleus—*e. g.*, benzodifurfurane and benzodipyrrol derivatives (p. 464).

Coumarone and *indol* should be especially mentioned as the parent substances of important groups. Indol is the mother substance of indigo. These two bodies will be considered together with benzothiophene. Next will follow the groups of dibenzo-compounds: diphenylene oxide, diphenylene sulphide, and carbazole.

5. BENZOFURFURANE or COUMARONE GROUP.

The coumarone compounds, as their name would imply, are produced:

(1) By the action of alcoholic potash upon coumarine dibromides or α-brom coumarines (Fittig, A. 216, 162):



α-Bromcoumarine — Coumarilic Acid — Coumarone.

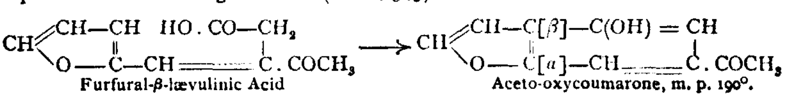
Other coumarines react similarly—*e. g.*, umbelliferone, æsculetine, and daphnetin.

It is very certain that α-brom-o-oxycinnamic acid and its homologues occur as intermediate products. These split off HBr and form the coumarone ring. The formation of benzoyl coumarone, $C_6H_4\left<\begin{matrix}CH\\ O\end{matrix}\right>C.COC_6H_5$, from aceto-o-oxybenzalacetophenone dibromide and caustic potash, as well as by the condensation of salicylaldehyde by means of ω-bromacetophenone and caustic potash, proceeds analogously (B. 29, 237, R. 290).

(2) Other o-disubstitution products of benzene combine to yield a coumarone ring. Caustic potash converts o-oxychlorstyrene into coumarone (B. 26, R. 678):

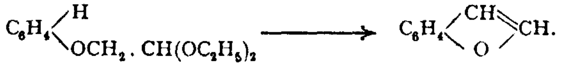
(3) By heating o-aldehydo-phenoxy-acetic acid with sodium acetate, coumarilic acid results (B. 17, 3000):

(4) The synthesis of aceto-oxycoumarone, however, from furfural-β-lævulinic acid represents a benzene ring formation (B. 26, 345):

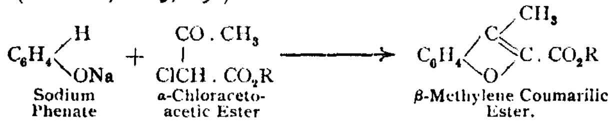


Furfural-β-lævulinic Acid — Aceto-oxycoumarone, m. p. 190°.

(5) By the action of zinc chloride upon phenoxylacetals and their homologues (B. 30, 1700):



(6) Just as the coumarines are formed from phenol and malic acid or acetoacetic ester, so the coumarones are obtained from the sodium salts of the phenols with *a* chloraceto-acetic ester (Hantzsch, B. 19, 1291):



Resorcin and two molecules of the ester yield a *benzodifurfurane*, pyrogallol with three molecules of the ester form a *benzotrifurfurane*, while a *naphthofurfurane* is obtained from naphthol.

A perfectly similar reaction is noticeable in the production of coumarone and benzodifurfurane derivatives from quinones and chlorinated quinones—*e. g.*, chloranil, when heated with acetoacetic ester (J. pr. Ch. [2], 45, 67; A. 283, 245).

Coumarone, C_8H_6O, boiling at 169°, is formed by distilling coumarilic acid with lime. It is obtained from o-oxy-ω-chlorstyrene; from phenoxylacetal with zinc chloride (B. 30, 1703), as well as from coal-tar (B. 23, 78). Concentrated acids convert it into a resin. With bromine it yields a *dibromide*, melting at 88°. Sodium and alcohol reduce it to **dihydrocoumarone,** *coumaran*, C_8H_8O, boiling at 189°, together with ethyl phenol (B. 25, 2409).

β-**Methyl Coumarone,** C_9H_8O, from methyl coumarilic acid, boils at 189°. *a*,*β*-**Dimethyl coumarone,** from dimethyl coumarilic acid, boils at 210°.

a-**Benzoyl Coumarone,** $C_8H_5O(COC_6H_5)$, melting at 91°, obtained from acetyl-o-oxybenzalacetophenone dibromide, as well as in the condensation of salicylaldehyde with phenacyl bromide, is decomposed by fusion with caustic potash into coumarone and benzoic acid (B. 29, 237, R. 290).

a-**Coumarilic Acid,** $C_8H_5O.COOH$, melting at 190°, is obtained from *a*-brom-coumarine. Sodium amalgam converts it into **hydrocoumarilic acid,** $C_9H_8O_3$.

β-**Methyl-*a*-coumarilic Acid** melts at 189°. Its *ethyl ester* is produced on heating sodium phenoxide with acetoacetic ester (see above). It melts at 51°.

1,2,4-Trichlor-3-oxy-*β*-methyl-coumarilic Acid, $C_6Cl_3(OH)\langle{}^{C(CH_3)}_{O}\rangle C.CO_2H$, melting at 258°, is prepared from chloranil and acetoacetic ester.

β-**Ketocoumaran,** *Ketodihydrocoumarone*, $C_6H_4<{}^{CO}_{O}>H$, melting at 97°, is made from aceto-o-oxyacetophenone bromide (B. 30, 1081).

Benzodimethyldifurfurane Dicarboxylic Ester,

$CO_2R.C\langle{}^{(CH_3)C}_{\quad O}\rangle C_6H_2\langle{}^{C(CH_3)}_{O\quad}\rangle C.CO_2R$, is obtained from resorcinol and chlor-acetoacetic ester. The *a*-compound melts at 186° and the *β*-body at 141°. **Benzo-trimethyltrifurfurane Tricarboxylic Ester,** $C_6\left\{{}^{C.CH_3}_{O>C.CO_2R}\right\}_3$, is similarly formed from phloroglucin. It melts with decomposition at 297°.

Naphthofurfurane, $C_{10}H_6[C_2H_2O]$, melting at 61°, is made by the action of $ZnCl_2$ upon naphthoxylacetaldehyde, $C_{10}H_7O.CH_2.CHO$, dissolved in glacial acetic acid (B. 30, 1702). **Naphthomethylfurfurane Carboxylic Ester,** $C_{10}H_6\langle{}^{C.CH_3}_{O}\rangle C.CO_2R$, melting at 110°, is obtained from *a*-naphthol and chloracetoacetic ester.

Naphthoketocoumaran, $C_{10}H_6(C_2H_2O_2)$, melting at 92°, is formed from 2-brom-aceto-1-acetylnaphthol (B. 30, 1468).

6. BENZOTHIOPHENE GROUP.

Benzothiophene is produced from α-sulphhydryl-ω-chlorstyrene, which has only been isolated in the form of its xanthogenic ester. This is analogous to the formation of coumarone from o-oxy-ω-chlorstyrene (B. **26**, 2809):

$$C_6H_4\left\langle\begin{matrix}CH = CHCl\\ SH\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}CH\\ S\end{matrix}\right\rangle CH;$$

which is similar to the formation of acetoxycoumarone from the condensation product of furfurol and lævulinic acid.

Oxybenzothiophene results from the condensation of thiophenaldehyde with succinic acid (B. **19**, 1619):

$$C_4H_2S\begin{cases}[\beta]H\\ [\alpha]CHO\end{cases} + \begin{matrix}HOOC.CH_2\\ |\\ H_2C—COOH\end{matrix} \longrightarrow C_4H_2S\begin{cases}[\beta]C(OH) = CH\\ [\alpha]CH \text{=====} CH\end{cases}(+ 2H_2O + CO_2)$$

Thiophenaldehyde — Succinic Acid — 4-Oxybenzothiophene.

Benzothiophene, Thionaphthene, C_8H_6S, melting at 31° and boiling at 221° (C. 1897, II, 270), has an odor like that of naphthalene. **4-Oxythionaphthene**, $C_8H_5(OH)S$, melting at 72°, resembles α-naphthol in its behavior (compare thiophene).

BENZPYRROL OR INDOL GROUP.

The most important substances belonging in this group have been obtained from *indigo-blue*, to which the indol derivatives bear an intimate kinship. Indol, and especially the methyl indols, as derivatives of pyrrol, show most of the reactions of the latter (B. **19**, 2988). By a rupture of the ring the indol bodies are converted mainly into orthoamido-acids of benzene. Our knowledge of the constitution of indol and its derivatives, and their relations to indigo, is based chiefly upon the investigations of A. v. Baeyer (p. 473).

Indol, $C_8H_7N = C_6H_4\left\langle\begin{matrix}CH\\ NH\end{matrix}\right\rangle CH\,(\alpha)$, melting at 52° and boiling at 245° with decomposition, is obtained:

(1) By the distillation of oxygen-containing derivatives—*e.g.*, oxindol (p. 471), indigo blue (p. 473)—with zinc-dust.

(2) By condensation of various o-amido-substitution products of benzene, or by the reduction of o-nitro-compounds; for example, the action of sodium alcoholate upon o-*amidochlorstyrene* (p. 207), $C_6H_4\left\langle\begin{matrix}CH = CHCl\\ NH_2\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}CH\\ NH\end{matrix}\right\rangle CH$, analogous to coumarone (p. 463) and benzothiophene (above); also by the reduction of o-*nitrophenylacetaldehyde* or o-*nitrocinnamic acid*, $C_6H_4\left\langle\begin{matrix}CH_2.CHO\\ NO_2\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}CH\\ NH\end{matrix}\right\rangle CH$.
It is very probable that the production of indol from *phenylglycocoll*, $C_6H_5NH.CH_2.COOH$, and calcium formate proceeds in a similar manner (B. **23**, R. 654).

(3) The pyrogenic formation of indol from alkylic anilines, tetrahydroquinoline, and especially from *cumidine* when the vapors are conducted through tubes heated to redness, are due to ortho-condensations.

(4) Finally, indol is formed (together with skatole—see this) from *albuminates* in the pancreatic fermentation (method of production), or when they are fused with caustic potash.

Behavior: Indol crystallizes from water in shining leaflets. It possesses a peculiar odor, resembling that of naphthylamine, and is readily volatilized in aqueous vapor. Its vapor density (under diminished pressure) corresponds to the formula C_8H_7N. A pine splinter moistened with hydrochloric acid and dipped into its alcoholic solution or the vapors acquires a cherry-red color. Indol possesses but very feeble basic properties (similar to pyrrol), and is easily resinified by acids.

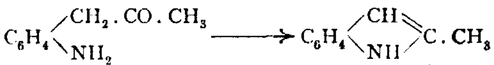
With picric acid it forms a compound which crystallizes in red needles.

The substituents of indol in the pyrrol ring are termed α-, β-, n-, or Py(1,2,3); those in the benzene ring, 1,2,3,4 or Bz(1,2,3,4) (A. 236, 121).

n-*Nitrosoïndol*, $C_7H_6N \cdot NO$, melting at 172°, formed from indol and sodium nitrite, probably has the doubled formula (C. 1891. II, 62). Various *acetyl indols* are produced when indol and acetic anhydride are heated together (B. 23, 1359, 2296).

Homologous Indols are produced:

1. Like indol from o-amido-compounds of the benzene series by the formation of closed rings:

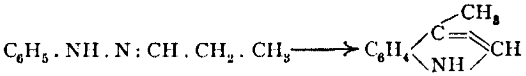


o-Amidobenzyl Methyl Ketone *α-Methyl Indol.*

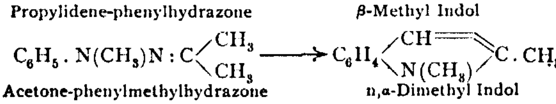
Similarly, o amido-desoxybenzoin yields α-phenyl indol and o-methylamido-ω-chlorstyrene: n-methyl indol.

2. By heating the anilines with compounds containing the group CO . CHCl. For example, aniline and chloracetone yield α-methyl indol; with β-bromlævulinic acid, α,β-dimethyl indol is the product. A simultaneous evolution of CO_2 occurs here. This reaction is parallel to that of the so-called *quinaldine synthesis*. For its course see B. 25, 2860; 26, 1336, 2638. Aniline and bromacetophenone yield α-phenyl indol.

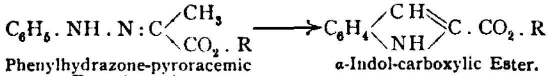
3. A noteworthy method for the production of the alkyl indols consists in condensing the phenylhydrazones of the aldehydes, ketones, and ketonic acids by heating them with hydrochloric acid or zinc chloride (E. Fischer, B. 19, 1563; 22, R. 14), when ammonia is split off:



Propylidene-phenylhydrazone β-Methyl Indol



Acetone-phenylmethylhydrazone n,α-Dimethyl Indol



Phenylhydrazone-pyroracemic Ester (p. 124) α-Indol-carboxylic Ester.

The unsym. alkylphenylhydrazine derivatives react very easily with pyroracemic acid upon warming them with dilute hydrochloric acid, sulphuric or phosphoric acid; the products are n-alkyl-indol-carboxylic acids. The phenylhydrazones of the β-ketonic acids—*e. g.*, acetoacetic ester—are principally converted into pyrazole compounds. Some, when heated with concentrated sulphuric acid, yield indol compounds (B. 27, R.

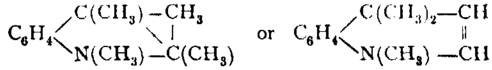
793). This is especially true of the unsym. alkylphenylhydrazones. See also indolinons, p. 470.

4. The polymeric alkyl pyrrols upon standing with dilute sulphuric acid part with ammonia and pass into alkylic indols—*e. g.*, tetramethyldipyrrol changes to α,β,2,3-tetramethyl indol.

Behavior: The alkyl indols substituted in the pyrrol nucleus possess generally the fæcal odor, and can be distilled without decomposition. The phenyl indols and indol carboxylic acids are non-volatile and odorless. They are more stable toward acids than indol, dissolve in concentrated acids, and are reprecipitated unaltered by water. Picric acid unites with all of them, forming compounds crystallizing in red needles. Most of the indol derivatives give the pine-shaving reaction, the exceptions being the indol carboxylic acids and the α,β-dialkyl indols. The alkyl indols, like the alkyl pyrrols, yield indol carboxylic acids when they are fused with caustic potash.

The indols, like pyrrol, combine with aldehydes, acid anhydrides, and diazo-compounds, hydrogen atoms of the pyrrol nucleus being replaced by the acidyl, the diazo-group, etc. *Red* dyestuffs, resembling fuchsine and called *rosindols* (B. **20**, 815), are produced by heating various indols with benzoyl chloride and zinc chloride.

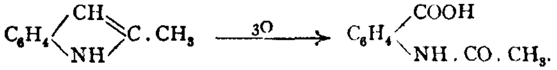
The behavior of indol by exhaustive methylation is remarkable: all of the hydrogen atoms of the pyrrol nucleus are replaced by methyl, and then by the further action of methyl iodide a body results which formerly was thought to be a dihydro-n,α,γ-trimethylquinoline, because its corresponding reduction product, a tetrahydro-base, could be changed to α,γ-dimethyl-quinoline. However, the so-called dihydrotrimethyl quinoline is reconverted by the distillation of its iodhydrate into α,β-n-trimethyl indol, and when oxidized with chromic acid or potassium permanganate yields β, β-dimethyl-α-indolinon, so that formulas like the following have been suggested:


(B. 29, 2460).

Compare B. 21, 1940, for the conversion of the indols into quinolines by means of chloroform and sodium alcoholate.

n-**Methyl Indol**, $C_8H_6N(CH_3)$, boiling at 239°; n-**Ethyl Indol**, boiling at 247°; **Allyl Indol**, boiling at 252° (B. 26, 2174); and n-**Phenyl Indol**, $C_8H_6N(C_6H_5)$, are obtained from their carboxylic acids by the elimination of carbon dioxide. Bromine in sodium hydroxide oxidizes n-methyl and n-ethyl indol to *methyl* and *ethyl-ψ-isatin* (p. 472).

α-**Methyl Indol**, $C_8H_6(CH_3)NH$, **Methyl Ketol**, arises from o-amido-benzyl-methyl ketone, and acetone phenylhydrazone. It melts at 59°. Its odor is like that of indol, and its reactions are similar. Oxidation with MnO_4K (by rupture of the pyrrol ring at the point of the double binding) converts it into o-aceto-amido-benzoic acid:



α-Indol carboxylic acid is formed when it is fused with caustic potash.

β-**Methyl Indol**, *Skatole*, $C_8H_5(CH_3)NH$, occurs in human fæces (with a little indol). It may be obtained, together with indol, from reduced indigo, by the putrefaction of albuminoids, or (with indol) in the fusion of the same with potassium hydroxide. It can be prepared without difficulty by heating propidene-phenylhydrazone with zinc chloride. It melts at 95° and boils at 265°. It has a penetrating fæcal odor.

n,α,β-**Trimethyl Indol** boils at 280° (see above). α,β,2,3-**Tetramethyl Indol**, $(CH_3)_2C_6H_2:[C_2(CH_3)_2NH]$, melts with decomposition at 285° (B. **22**, 1924). It is obtained from tetramethyldipyrrol (p. 458). α-**Phenyl Indol**, $C_8H_5(C_6H_5)NH$, melting at 187°, has been prepared from acetophenone phenylhydrazone, from o-nitrodesoxybenzoïn, from bromacetophenone and aniline (see above), and, lastly, by the rearrangement of β-**Phenyl Indol**, $C_8H_5(C_6H_5)NH$, melting at 89°, upon heating it to 170° with zinc chloride (B. **21**, 1811). Similar rearrangements are manifested by the different *methyl phenyl indols* (B. **22**, R. 44). α-**Thiënyl Indol**, melting at 162°, and α-**Naphthyl Indol**, melting at 196°, are obtained from the phenylhydrazones of naphthyl and thiënylmethyl ketones (B. **26**, R. 44).

2. The *chlorine substitution* products of the indols are produced by the action of PCl_5 upon their oxygen containing derivatives—*e. g.*, α,β-**dichlorindol**, $C_8H_4Cl_2NH$, melting at 104°, from oxindol (p. 471).

3. **Sulphoacids** of the indols, containing the sulpho-group in the pyrrol-nucleus, have been synthesized from methyl and ethyl aniline by condensation with *glyoxal bisulphite* (1, 321) (B. **27**, 3258):

n-**Methyl Indol**-α-**Sulphonic Acid**, $C_6H_4\langle\begin{matrix}CH\\N(CH_3)\end{matrix}\rangle C.SO_3H$, on being boiled with hydrochloric acid, splits off SO_2 very readily and becomes n-*methyl oxindol*. The naphthylamines and alkylic naphthylamines react like the alkylic anilines with glyoxal bisulphite.

4. *Indol Carboxylic Acids.*

These are produced (1), in addition to the synthetic method, from the phenylhydrazones of the pyroracemic acids, by reactions perfectly similar to those employed for the pyrrolcarboxylic acids; (2) when the indols are heated with sodium and carbon dioxide; (3) by fusing the alkyl indols with caustic alkali. Ordinary oxidizing agents do not attack them (B. **21**, 1925). Heated alone or with lime, they break down into carbon dioxide and indols.

α-**Indol Carboxylic Acid**, $C_8H_6N.CO_2H$, melting at 200° with decomposition, has been prepared from pyroracemic phenylhydrazone, from α-methyl indol by the potash fusion, and by the latter process from *tetrahydrocarbazole*.

The acid also results in the reduction of o-nitrophenyl pyroracemic acid with zinc-dust and glacial acetic acid, whereas the product will be n-oxyindolcarboxylic acid when sodium amalgam is used (see p. 469 and B. **30**, 1045). It yields an *imide* anhydride (B. **22**, 2503) corresponding to *pyrocoll* if heated with acetic anhydride.

β-**Methyl**-α-**Indol Carboxylic Acid**, $C_8H_5(CH_3)N.CO_2H$, *skatole carboxylic acid*, results from the decay of albuminates. It melts at 165°. Another product, formed at the same time, is **Skatole Acetic Acid**, $C_8H_5(CH_3)N.CH_2.CO_2H$, melting at 134° (B. **22**, R. 701).

β-**Indol Carboxylic Acid**, $C_8H_6N.CO_2H$, is produced when skatole is fused with caustic potash, and upon heating indol with sodium in a current of carbon dioxide. It melts with decomposition at 218°. It does not yield an imide anhydride (B. **23**, 2296).

n-α-*Dimethyl-indol-β carboxylic acid*, $C_8H_4(\overset{\alpha}{CH_3})N(\overset{\beta}{CH_3}).COOH$, from methyl-phenylhydrazone acetoacetic ester, $C_6H_5N(CH_3).N:C(CH_3).CH_2.CO_2R$, melts at 200°.

5. *Oxyindol Derivatives:* **Indoxyl**, β-**Oxyindol**, $C_6H_4\langle\begin{matrix}C(OH)\\NH\end{matrix}\rangle CH$, from indoxylic acid by the elimination of CO_2, and from indigo by fusion with caustic potash away from air (B **26**, 225), is an oil easily soluble in water, with a yellow fluorescence. It is very unstable and is readily resinified. It dissolves with a red color in concentrated hydrochloric acid. It is oxidized to *indigo blue* when its alkaline solution (best ammoniacal) is exposed to the air. Ferric chloride and hydrochloric acid effect the conversion more quickly:

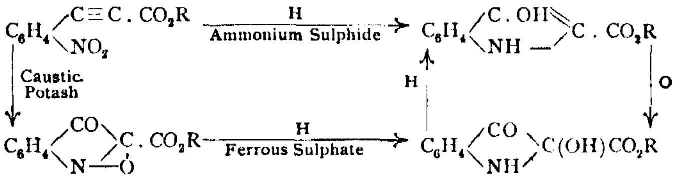
$$2C_8H_7ON + 2O = \underset{\text{Indigo Blue.}}{(C_8H_5NO)_2} + 2H_2O.$$

When indoxyl is digested with potassium pyrosulphate, $S_2O_7K_2$, we get *potassium indoxylsulphate*, $C_8H_6N.O.SO_3K$, which is found in the urine of herbivorous ani-

mals (*Urine indican*), generally after the ingestion of indol. When digested with acids the salt decomposes into sulphuric acid and indoxyl, which forms indigo blue by the addition of a little ferric chloride. We proceed similarly in the detection of indoxyl-sulphuric acid in urine.

This potassium salt may be synthesized by fusing o-phenylglycocoll-carboxylic acid with caustic potash, and subsequently treating with potassium pyrosulphate. If the potassium hydrate fusion be treated with benzyl chloride, n-**Benzyl-β-benzyl-oxyindol,** melting at 166°, is produced (C. 1897, I, 862).

Indoxylic Acid, $C_9H_7NO_3 = C_6H_4\left<\begin{matrix}C(OH)\\NH\end{matrix}\right>C.CO_2H$, a carboxylic acid of indoxyl, is produced from its ethyl ester by fusion with caustic soda (B. 17, 976). It melts at 123°, with decomposition. Its *ethyl ester* is obtained by reducing o-nitrophenyl propiolic ester with ammonium sulphide, or isatogenic ester, and from indoxanthic ester, which is an intermediate product in this reaction, and can be obtained by oxidizing the ester of indoxylic acid:



Isatogenic Ester, m.p. 151° Indoxanthic Ester (B. 15, 744).

When digested with sulphuric acid it affords a quantitative yield of *indigo-sulphonic acid*. It possesses a phenol character, which is indicated by its solution in alkalies, from which it is again precipitated by carbon dioxide. Ethyl iodide converts the salts of indoxylic ester into ethyl indoxylic ester, $C_8H_5(OC_2H_5)N.CO_2R$, which by saponification with baryta water, forms **Ethyl-indoxylic Acid.** This acid loses CO_2 when it is heated, and becomes **ethyl indoxyl,** $C_8H_6(OC_2H_5)N$, which resembles indol in its chemical behavior and in its odor. When digested with hydrochloric acid, ethyl indoxylic acid yields *indoxyl*, and by nitrous acid is converted into *pseudoisatoxime* (p. 472).

In many reactions indoxyl, as well as indoxylic acid, yields products which are derived from **pseudoïndoxyl,** or *dihydro-β-ketoïndol*, an isomeride of indoxyl, so that it may be assumed that in these instances

$C_6H_4\left<\begin{matrix}C.OH\\NH\end{matrix}\right>CH$ changes to $C_6H_4\left<\begin{matrix}CO\\NH\end{matrix}\right>CH_2$ (compare dihydroresorcinol, p. 296; phloroglucin, p. 165, etc.).

In the second form indoxyl and indoxylic acid react with aldehydes, ketones, and ketonic acids,—*e. g.*, benzaldehyde, pyroracemic acid, etc.,—with the production of so-called **indogenides.** The bivalent group, $C_6H_4<^{CO}_{NH}>C=$, is termed *indogen* (B. 16, 2197):

$$C_6H_4<^{CO}_{NH}>C=CH.C_6H_5 \qquad C_6H_5<^{CO}_{NH}>C=C(CH_3)CO_2H$$

Indogenide of Benzaldehyde Indogenide of Pyroracemic Acid.

Isatin and benzene hydrocarbons also yield indogenides. Isatin may be viewed as *indogen oxide*. Isatin converts indoxyl (B. 17, 976) into the indogenide **indirubin** (p. 476):

$$C_6H_4<^{CO}_{NH}>CH_2 + OC<^{C_6H_4}_{CO}>NH \longrightarrow C_6H_4<^{CO}_{NH}>C=C<^{C_6H_4}_{CO}>NH$$

ψ-Indoxyl Isatin Indirubin.

which is isomeric with indigo blue. The latter is also produced by the oxidation of indoxyl (p. 468); hence it may be viewed as **diindogen**:

$$C_6H_4{<}\substack{CO\\NH}{>}C = C{<}\substack{CO\\NH}{>}C_6H_4.$$

Indigo Blue (Diindogen).

β-Ethoxy-α-methyl Indol, $C_8H_5N(O.C_2H_5)(CH_3)$, melting at 142°, is obtained from ethoxyacetonephenylhydrazone, $C_6H_5NHN:C(CH_3)CH_2OC_2H_5$ (B. **25**, R. 417).

n-**Oxyindol-α-carboxylic Acid**, melting at 159° with decomposition, is isomeric with indoxylic acid. It results on boiling o-nitrobenzylmalonic acid with sodium hydroxide:

$$C_6H_4{<}\substack{NO_2\\CH_2-CH(COOH)_2}\longrightarrow C_6H_4{<}\substack{N(OH)\\CH=}{>}C(COOH),$$

as well as by the reduction of o-nitrophenylpyroracemic acid with sodium amalgam. It is readily reduced to α-indol carboxylic acid. Potassium permanganate oxidizes it, with the possible intermediate production of phenylhydroxylamine-o-carboxylic acid, to o-azoxybenzoic acid, while with chromic acid it yields isatin. It can be very easily acidylated or alkylized in the NOH-group.

n-**Methoxyindol-α-carboxylic Acid**, melting at 185° with decomposition, is also reduced to indolcarboxylic acid, and oxidized by chromic acid to **n-Methoxy-ψ-isatin**, $C_6H_4{<}\substack{CO\\N(OCH_3)}{>}CO$, consisting of red needles, melting at 110°. Bleaching lime, hydrogen peroxide, etc., convert n-oxyindolcarboxylic acid into **indoxin**. This is a blue-colored, unstable dye, very similar to indigo, but soluble in alkalies. When it is dissolved in concentrated sulphuric acid and the diluted solution is allowed to stand exposed to the air, **indigo** separates. The yield is good (B. **29**, 639; **30**, 1045, 1052).

α-**Phenyl-oxyindol**, $C_8H_5N(C_6H_5)(OH)$, melting at 175°, is formed in the action of concentrated sulphuric acid upon benzoïn oxime. It is doubtful whether in this derivative the hydroxyl group is attached to the nitrogen or to one of the C-atoms (see B. **29**, 2062).

Hydroïndol Derivatives: A hydro-derivative of indol itself is not known. However, when the alkyl indols are reduced with tin and hydrochloric acid, dihydro-derivatives have been produced. Thus, α-methyl indol (methyl ketol) yielded **dihydromethyl ketol**, $C_6H_4{<}\substack{CH_2\\NH}{>}CH.CH_3$, boiling at 227°. Its behavior differs greatly from that of the mother substance. In its properties it is closely allied to the *alkylic anilines*. In its relations to tetrahydroquinaldine, which contains the six-membered hydrogenized pyridine ring condensed with the benzene ring, it behaves like ethyl- to propyl-aniline (*cyclic homology*, B. **26**, 1285). Silver sulphate oxidizes dihydromethyl ketol back to methyl ketol (B. **27**, 827). Malonic ester and dihydromethyl ketol form a tricyclic condensation product (B. **26**, 1298):

$$C_6H_4{<}\substack{CH_2\\NH}{>}CH.CH_3 + \substack{ROOC\\ROOC}{>}CH_2 \longrightarrow \begin{matrix}CO-C_6H_3{<}\substack{CH_2\\N-}{>}CH.CH_3,\\ | \qquad\qquad\quad |\\ CH_2 \text{------} CO\end{matrix}$$

which can also be regarded as a derivative of a diketotetrahydroquinoline (see this).

α,α-**Dimethyldihydroïndol**, $C_6H_4{<}\substack{CH_2\\NH}{>}C:(CH_3)_2$, boiling at 210°, is readily produced by distilling o-isopropylamidobenzyl alcohol, $C_6H_4{<}\substack{CH_2.OH\\NH.CH(CH_3)_2}$.

Oxygen-containing Dihydroindol Derivatives.

Dihydroketoïndols or Indolinons have been prepared by the condensation of acidyl methylphenylhydrazides by means of lime:

$$C_6H_5N(CH_3)NH.CO.CH(CH_3)_2 \xrightarrow{-NH_3} C_6H_4{<}\substack{C(CH_3)_2\\N(CH_3)}{>}CO.$$

n,β,β-Trimethyl Indolinon, melting at 50° (25°) and boiling at 265°, is formed from isobutyrylmethylphenylhydrazide, and may also be prepared by oxidizing the base $C_{11}H_{15}NO$, resulting from the condensation of isobutylidenemethylphenylhydrazine with alcoholic zinc chloride, with an ammoniacal silver solution. Further, trimethylindolinon has also been produced by oxidizing the so-called trimethyldihydroquinoline from indol (see p. 468). When reduced it again yields the base $C_{11}H_{15}NO$, which is therefore probably **Trimethyl-α-oxyindolin** (compare C. 1897, II, 120). **n,β-Dimethylindolinon**, $C_6H_4[C_2HNO(CH_3)_2]$, melting at 23° and boiling at 273–277°, is formed from **Propionylmethylphenylhydrazide** (M. 17, 479).

The anhydrides or lactams of some of the o-amido-acids of benzene belong here. They have been previously described, but because of their intimate relationship to indol will be again brought together:

1. Lactam of o-amidophenylacetic acid. This is *oxindol* or α-keto-dihydroïndol (β-ketodihydroïndol is the ψ-indoxyl which was just described above).

2. Lactam of o-amidomandelic acid. This is *dioxindol* or α-keto-β-oxyhydroïndol.

3. Lactam (or lactime) of o amidobenzoyl formic acid. This is *isatin* or *α,β-diketohydroïndol.*

These compounds change readily into one another as a result of reduction or oxidation:

1. **Oxindol**, $C_8H_5NO = C_6H_4\langle{}^{CH_2}_{NH}\rangle CO$. Its properties have been given on p. 214. It was first obtained by the reduction of dioxindol; and in a moist condition, on exposure to air readily reoxidizes to the latter. It therefore reduces an ammoniacal silver solution. Nitrogen trioxide converts it into isatoxime (p. 472). By reduction the latter becomes **amido-oxindol** and this isatin by oxidation:

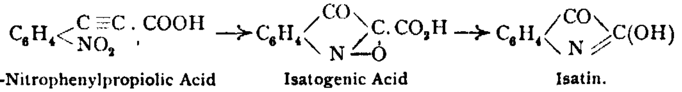
$$C_6H_4\langle{}^{CH_2}_{NH}\rangle CO \xrightarrow{N_2O_3} C_6H_4\langle{}^{C:(NOH)}_{NH}\rangle CO \xrightarrow{H} C_6H_4\langle{}^{CH(NH_2)}_{NH}\rangle CO \xrightarrow{O} C_6H_4\langle{}^{CO}_{NH}\rangle CO$$

Oxindol — Isatoxime — Amido-oxindol — Isatin.

Di-oxindol, $C_6H_4\langle{}^{CH(OH)}_{NH}\rangle CO$. Its properties are given on p. 251. It is readily obtained by boiling isatin with zinc-dust and hydrochloric acid. It oxidizes readily in aqueous solution to *isatid* and *isatin*. It is also obtained by the reduction of indigo.

3. **Isatin**, $C_6H_4\langle{}^{CO}_{NH}\rangle CO$, or $C_6H_4\langle{}^{CO}_{N}\rangle C.OH$. Its properties are given on p. 258. The following methods for its formation may be especially mentioned:

1. The oxidation of indigo with nitric acid (*Method of preparation*, J. pr. Ch. [2], 24, 11; 25, 434).
2. The oxidation of *oxindol* and *dioxindol.*
3. The action of alkali upon o-*nitrophenylpropiolic acid*, when there occurs at first a rearrangement into *isatogenic acid*, which then loses carbon dioxide and becomes isatin:



o-Nitrophenylpropiolic Acid — Isatogenic Acid — Isatin.

If a reducing agent be added to the alkaline solution of the o-nitrophenylpropiolic acid, *indigo* will result instead of isatin (see below).

Behavior:

(1) *Isatoic Acid*, $C_6H_4\langle{}^{N.COOH}_{CO}$, is formed when isatin is oxidized with chromic acid in glacial acetic acid solution.

Isatin yields *nitrosalicylic acid* when oxidized with nitric acid. (2) When reduced with ammonium sulphide we get first **isatid**, $C_{16}H_{12}N_2O_4$, then dioxindol and oxindol.

(3) Ammonia and primary amines form **Imesatins** of the general formula $C_6H_4\langle{}^{C=NR}_{NH}\rangle CO$, which, when digested with alkalies, decompose again into isatin and amines.

o-Phenylenediamine yields *indophenazine* (B. **29**, 194, 1030); piperidine yields a *dipiperidyl isatin*, $C_8H_5NO(NC_5H_{10})_2$, which can be converted into a dye—*isatin blue*—similar to indigo (B. **24**, 1366). (4) Isatin condenses, further, with benzene hydrocarbons, phenols, etc. Water exit occurs. It forms with thiophene the blue dye *indophenin*, $(C_8H_5NO_2 + C_4H_4S - H_2O)$. Similar products are obtained with furfurane and pyrrol. (5) The hydroxyl or lactime formula of isatin furnishes alkali salts; from the solution of the latter silver nitrate precipitates **silver isatin**, $C_8H_4(OAg)NO$, with which alkyl iodides yield O-alkyl isatins: **Methyl Isatin**, $C_8H_4(OCH_3)NO$, melting at 102°; **Ethyl Isatin**, $C_8H_4(OC_2H_5)NO$, melting at 88°, which can be resaponified to isatin or isatinates. (6) The keto- (lactam or pseudo-) form of isatin yields: **n-Methyl-ψ-isatin**, $C_6H_4:(C_2O_2N—CH_3)$, melting at 134°, and **n-Ethyl-ψ-isatin**, melting at 95°. These are obtained by the action of NaOBr upon n-methyl and n-ethyl indol (p. 467). The second compound is also formed from ethyl-ψ-isatin ethyloxime (see below). **n-Acetyl-ψ-isatin**, $C_6H_4:(C_2O_2C.C_2H_3O)$ (p. 258), is obtained from isatin and acetic anhydride. (7) Similarly, *two isomeric isonitroso-compounds* are derived from isatin: isatoxime and pseudoisatoxime.

Isatoxime, $C_6H_4\langle{}^{C=NOH}_{N}\rangle COH$, melts at 202°, with decomposition. It is prepared from isatin and hydroxylamine; or from oxindol by action of nitrous acid, and when reduced it yields so-called amido-oxindol, which can be oxidized to isatin. By the successive action of ethyl iodide upon the silver salt we obtain a *mono-* and a *diethyl* derivative from which isatin (B. **16**, 1706) is formed after saponification, which would indicate that the ethyl groups are combined with oxygen.

Pseudo-isatoxime, $C_6H_4\langle{}^{CO}_{NH}\rangle C=N.OH$, melting with decomposition at 200°, is prepared by the action of nitrous acid upon ethyl indoxylic acid. Ethyl iodide converts it into (1) a *mono-* and (2) a *diethyl* derivative. The first alone yields isatin, whereas the second is converted into n-methyl-ψ-isatin:

$$\text{I. } C_6H_4\langle{}^{CO.C(N.O.C_2H_5)}_{NH}\quad \text{and} \quad \text{II. } C_6H_4\langle{}^{CO.C(N.O.C_2H_5)}_{N.C_2H_5}$$

Pseudoisatin-ethoxime n-Ethyl-ψ-isatin-ethoxime.

The reduction of n-ethyl-ψ-isatin-ethoxime produces *n-diethyl indigo* (B. **16**, 2201).

A dioxime is formed by n-acetyl-ψ-isatin and hydroxylamine. See B. **29**, 1030, for **isatin semicarbazone**, $C_8H_5NO(:NNHCONH_2)$.

8. Isatin Chloride, $C_6H_4\langle{}^{CO}_{N}\rangle CCl$, melting with decomposition at 180°, is produced by digesting isatin with PCl_5 in benzene solution. It dissolves with a blue color in ether. It is reduced in glacial acetic acid solution by hydriodic acid or by zinc-dust to *indigo-blue*:

$$2C_6H_4\langle{}^{CO}_{N}\rangle CCl \xrightarrow{4H} C_6H_4\langle{}^{CO.C:C.CO}_{NH\quad HN}\rangle C_6H_4 + 2HCl.$$

We can also obtain from the isatins substituted in the benzene nucleus substitution products of indigo-blue: *dibrom-*, *dinitro-*, and *dimethyl indigo-blue*.

Indigo-blue (*Indigotin*), $C_6H_4<{CO \atop NH}>C=C<{CO \atop NH}>C_6H_4$, constitutes the principal ingredient of commercial **Indigo,** derived from different *Indigoferæ* and from woad (*Isatis tinctoria*). It occurs in these plants as a glucoside, called *indican*, which parts with its variety of glucose and becomes indigo-blue, when boiled with dilute acids, or if acted upon with a ferment (if the various portions of the plant be covered with water and exposed to the action of the air). The indigo-blue separates in the form of a powder.

Commercial indigo contains, in addition to 20–90 per cent. of indigo-blue, various other substances, which have not been well studied, like *indigo gluten*, *indigo-brown*, and *indigo-red*, which are removed by successive treatment with dilute acetic acid, caustic potash, and hot alcohol.

A better procedure consists in first reducing indigo by means of grape-sugar and sodium hydroxide to soluble indigo-white, which can then be oxidized to indigo blue by the exposure of the alkaline solution to the air, when the indigo blue will separate in a pure condition (A. **195**, 305).

History: Indigo was in ancient times highly prized as a dye by the Oriental nations (Dioscorides, Pliny: ἰνδικόν, indicum). In Europe it found general application in dyeing, from the opening up of sea-intercourse with the East Indies to the 16th century. To-day the production of indigo from plants, chiefly in Bengal, Java, Central America, is about 8,300,000 kg., equivalent in money to about $20,000,000.

In the period of the alchemists indigo was quite frequently considered in Europe as a mineral or metal (compare Schultz: Steinkohlentheer, 2 Aufl. II, 883), presumably because of its copper-like lustre. More careful investigations into its chemical nature were first instituted in this century. Erdmann and Laurent observed simultaneously (1841) that nitric acid oxidized indigo to isatin, while Fritzsche found (1848) that aniline resulted when it was distilled with caustic potash. Baeyer and Knop (1865) reduced it to dioxindol, oxindol, and indol. The latter body Baeyer and Emerling (1869) obtained synthetically from o-nitrocinnamic acid, and when Nencki (1874) succeeded in oxidizing indol to indigo with ozone, the first synthesis of this interesting compound was achieved (compare, however, Engler, B. **28**, 312). Baeyer and his students (1870–'78) demonstrated the constitution and synthesis of oxindol or o-amidophenyl acetic acid lactam, its conversion into isatin, as well as various methods for the conversion of isatin into indigo blue. Claisen and Shadwell (1879) also obtained isatin from o-amidobenzoyl formic acid. Baeyer (1880–'82), by a series of new syntheses of indigo, produced more certain evidence of its constitution and found easy methods for its production. These, and even later syntheses, have, however, not succeeded in fulfilling technical expectations.

Syntheses of Indigo-blue: Different methods of producing indigo have been presented in the preceding paragraphs. A particularly easy procedure is (1) the oxidation of *indoxyl* (p. 468) with ferric chloride and hydrochloric acid:

$$2C_6H_4\left<{C(OH) \atop NH}\right>CH + 2O = C_6H_4\left<{CO \atop NH}\right>C = C\left<{CO \atop NH}\right>C_6H_4 + 2H_2O,$$

as well as (2) the reduction of *isatin chloride* (p. 472):

$$2C_6H_4\left<{CO \atop N}\right>CCl + 4H = C_6H_4\left<{CO \atop NH}\right>C = C\left<{CO \atop NH}\right>C_6H_4 + 2HCl.$$

Syntheses 3, 4, and 5 commence with o-*nitrocinnamic acid*, which can be prepared in the following manner from the elements:

Acetylene, synthesized from carbon and hydrogen, polymerizes to benzene. Brombenzene with methyl iodide and sodium yields toluene, which chromyl chloride or something of that nature will convert into benzaldehyde. The latter is changed by acetic anhydride and sodium acetate into cinnamic acid, which upon nitration is mainly changed to o-nitrocinnamic acid:

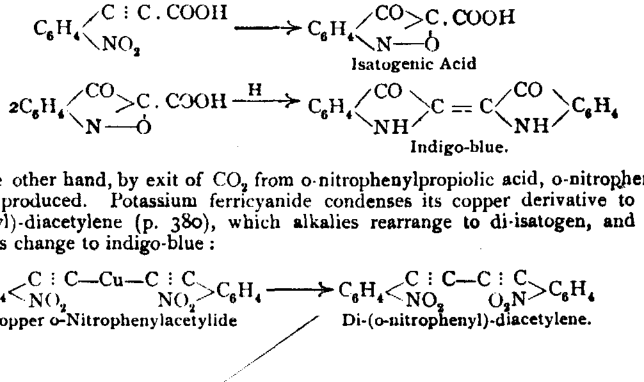
$$CH{\equiv}CH \rightarrow C_6H_6 \rightarrow C_6H_5Br \rightarrow C_6H_5.CH_3 \rightarrow C_6H_5CHO \rightarrow C_6H_5CH{:}CH.COOH \rightarrow C_6H_4\begin{cases}[1]NO_2\\ [2]CH{:}CH.COOH.\end{cases}$$

3. Potassium permanganate oxidizes o-nitrocinnamic acid to o-nitrobenzaldehyde, which condenses with acetone to o-*nitrophenyl lactic acid methyl ketone*. The alkalies decompose this ketone quite readily into acetic acid, water, and indigo-blue:

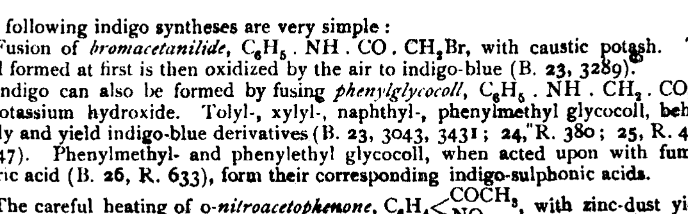
$$2C_6H_4{<}^{CH(OH).CH_2.CO.CH_3}_{NO_2} = C_6H_4{<}^{CO}_{NH}{>}C=C{<}^{CO}_{NH}{>}C_6H_4 + 2CH_3COOH + 2H_2O.$$

o-Nitrophenyl Lactic Acid Ketone — Indigo-blue.

4. o-Nitrocinnamic acid is changed by means of the dibromide into o-nitrophenylpropiolic acid. Alkaline reducing agents cause a rearrangement to isatogenic acid, and then, by the elimination of carbon dioxide, produce indigo:



5. On the other hand, by exit of CO_2 from o-nitrophenylpropiolic acid, o-nitrophenyl acetylene is produced. Potassium ferricyanide condenses its copper derivative to di-(o-nitrophenyl)-diacetylene (p. 380), which alkalies rearrange to di-isatogen, and reducing agents change to indigo-blue:



The following indigo syntheses are very simple:

6. Fusion of *bromacetanilide*, $C_6H_5.NH.CO.CH_2Br$, with caustic potash. The indoxyl formed at first is then oxidized by the air to indigo-blue (B. 23, 3289).

7. Indigo can also be formed by fusing *phenylglycocoll*, $C_6H_5.NH.CH_2.CO_2H$, with potassium hydroxide. Tolyl-, xylyl-, naphthyl-, phenylmethyl glycocoll, behave similarly and yield indigo-blue derivatives (B. 23, 3043, 3431; 24, R. 380; 25, R. 488; 26, 2547). Phenylmethyl- and phenylethyl glycocoll, when acted upon with fuming sulphuric acid (B. 26, R. 633), form their corresponding indigo-sulphonic acids.

8. The careful heating of o-*nitroacetophenone*, $C_6H_4{<}^{COCH_3}_{NO_2}$, with zinc-dust yields a sublimate of indigo-blue (B. 28, 309).

Benzylidene-o-nitroacetophenone, $C_6H_4<{COCH : CH . C_6H_5 \atop NO_2}$, readily breaks down under the influence of sunlight into indigo-blue and benzoic acid (B. **28**, 2497).

9. The production of indigo when ethylene anthranilic acid, $C_6H_4<{NH . CH_2 . CH_2 . NH \atop COOH \qquad\quad HOOC}>C_6H_4$, is fused with caustic potash belongs to this class of syntheses (B. **28**, 1685).

Constitution of Indigo-blue: The formula adopted for indigo is based upon the following facts:

1. The vapor density corresponds to the molecular formula $C_{16}H_{10}N_2O_2$.

2. The ready formation of indigo-blue from indoxyl and isatin, as well as its easy conversion into these bodies and into other indol derivatives, is an argument in favor of the view that the indigo formula is produced by the union of two groups, $C_6H_4<{C \atop N}>C:$

3. That these two residues must be linked to each other by C-union is evidenced by the synthesis from di-(o-nitrophenyl)-diacetylene (see above), which would indicate that diphenyl diacetylene, $C_6H_5C : C — C : C . C_6H_5$, is the parent hydrocarbon of indigo (see p. 380).

4. The formation of n-diethyl indigo from n-ethyl-ψ-isatin shows the presence of NH-groups (p. 472).

Properties: Indigo-blue is a dark-blue powder with a reddish glimmer; it becomes metallic and copper-like under pressure. It sublimes in copper-red, metallic, shining prisms. It is insoluble in water, alcohol, and ether, in alkalies and dilute acids, and is odorless and tasteless. It dissolves in hot aniline with a blue, in molten paraffin with a purple-red, color (this deportment recalls the various colors of iodine solutions), and can be crystallized from these solvents. It crystallizes from hot oil of turpentine in beautiful blue plates. Heated at the ordinary pressure it partially decomposes and is converted into a dark-red vapor. The same occurs with decomposition under 30–40 mm. pressure. See B. **18**, 1426, for the absorption spectrum of indigo and its derivatives.

Goods (wool) are dyed in two ways with indigo: (1) the wool is immersed in the aqueous solution of indigotin sulphonic acid, which fixes itself directly (Saxony-blue dyeing), or (2) the indigo-blue is changed by fermentation to indigo-white (indigo-vat), the cloth saturated with the latter and exposed to the air, when indigo-blue forms and sets itself upon the fibre. (3) In printing, a mixture of o-nitrophenylpropiolic acid and an alkaline reducing agent are sometimes substituted for the indigo. Steaming causes the formation of indigo-blue.

(4) Recently the bisulphite derivative of o-nitrophenyl-lactic acid ketone has been used with considerable success as the *indigo salt*. When printed in mixture with alkali and then steamed, it changes to indigo-blue.

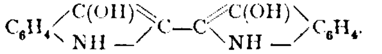
Derivatives of Indigo-blue: **Dichlor-, dibrom-, dinitro-indigos**, have been obtained from substituted isatins and o-nitroacetophenones (see methods of formation 2 and 8). Bz-3,5-**Dimethyl Indigo**, $(CH_3)C_6H_3(C_4O_2N_2H_2)C_6H_3(CH_3)$, is formed from o-nitro-m-toluic aldehyde (compare method of formation 3, p. 471). n-**Diethyl Indigo**, $(C_6H_4 : C_2ON . C_2H_5)_2$, is produced from n-ethyl-ψ isatin ethyloxime (p. 472).

α- and β-**Naphthyl Indigo**, $(C_{10}H_6 : C_2ONH)_2$, are produced by melting together the naphthylamines with chloracetic acid and caustic potash and then oxidizing in accordance with method 7 for the production of indigo-blue (B. **26**, 2547).

Indigo dissolves in concentrated sulphuric acid with a green color. After the solution has been digested for some time **indigotin monosulphonic acid,** *phoenicin sulphuric acid,* $C_{16}H_9N_2O_2 . SO_3H$, is produced. Water precipitates it from its solution in the form of a blue powder. It forms salts with a purple-red color; these are soluble in water. **Indigotin Disulphonic Acid,** $C_{16}H_8N_2O_2(SO_3H)_2$, is formed by the action of fuming sulphuric acid. It forms alkali salts which dissolve with difficulty in salt solutions, and occur in trade as *indigo carmine* in paste form.

Indigo Dicarboxylic Acid, $C_{16}H_8N_2O_2(COOH)_2$, is obtained from o-nitrophthalaldehydic acid, $C_6H_3(COOH)<^{COOH}_{NO_2}$, just as indigo is prepared from o-nitrobenzaldehyde.

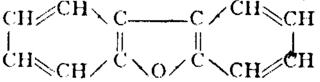
Indigo-white, $C_{16}H_{12}N_2O_2$, is obtained by the reduction of indigo-blue (see above). It can be precipitated from its alkaline solution by hydrochloric acid (air being excluded) as a white crystalline powder, soluble in alcohol, ether, and the alkalies, with a yellowish color. As it results from indigo by the absorption of two hydrogen atoms, and because of its phenol-like nature, it is ascribed the formula of a *di-indoxyl:*

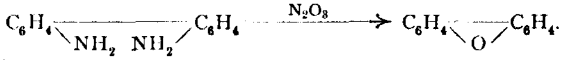


It rapidly re-oxidizes to indigo-blue by exposure to the air. It yields di-indol when heated with baryta-water and zinc-dust.

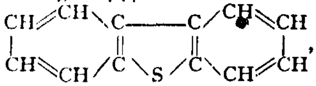
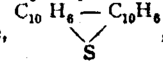
Indigo-red and *indigo purpurin* are isomerides of indigo-blue. The first occurs in commercial indigo, while the second is produced, together with indigo, from isatin chloride.

Indirubin, the indogenide of pseudoisatin, and *indin,* formed from isatid by fusion with caustic potash, or from dioxindol, are identical with indigo purpurin (B. 28, 540).

8. **Dibenzofurfurane, Diphenylene Oxide,**  melting at 81° and boiling at 288°, occurs in small quantities in "stubb-fat," and may be obtained synthetically (1) by distilling phenyl phosphate (p. 147) with lime; (2) by the same treatment of phenol with lead oxide; (3) on conducting phenyl ether through tubes heated to redness; (4) by decomposing the diazo-derivative of o-amido-phenyl ether with sulphuric acid (compare p. 147 and B. 29, 1876); and best by the action of dilute acids upon the tetrazo-compound of o_2-diamido-diphenyl (p. 337) (B. 25, 2746):

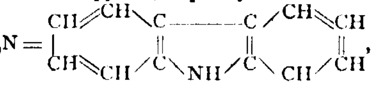


Bromine converts diphenylene oxide into **dibromdiphenylene oxide,** melting at 185°. Fuming nitric acid changes to **dinitrodiphenylene oxide,** melting at 200°. **Diamidodiphenylene oxide,** melting at 188°, yields valuable substantive azo-dyes (p. 338). **Acetyldiphenylene oxide** melts at 81°; see B. 24, R. 744.

9. **Dibenzothiophene, Diphenylene Sulphide,**  melting at 97° and boiling at 333°, is produced when phenyl disulphide, $(C_6H_5)_2S_2$, and phenyl sulphide, $(C_6H_5)_2S$, are distilled through tubes heated to redness. Chromic acid oxidizes it, in contradistinction to thiophene (p. 453), to **diphenylene sulphone,** $(C_6H_4)_2SO_2$, melting at 230°. **Dinaphthylene Thiophene,** , melting

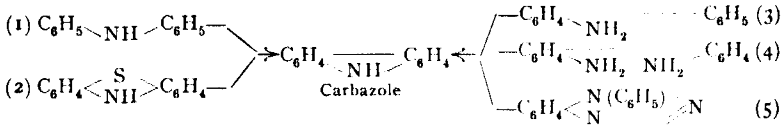
at 147°, is constituted analogously to dibenzothiophene. It results when concentrated sulphuric acid acts upon dioxydinaphthylene sulphide (B. 27, 3002).

10. **Dibenzopyrrol, Diphenyleneimide** or **Carbazole**,

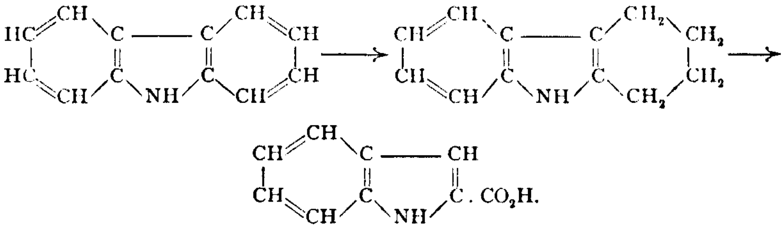
$C_{12}H_9N =$  , melting at 238° and boiling at 351°,

occurs in crude anthracene. It is withdrawn from it as carbazole-potassium by fusion with caustic potash. It may be synthesized:

(1) By conducting diphenylamine through tubes heated to redness; (2) by heating thiodiphenylamine with copper in powder form; (3) by distilling o-amidodiphenyl with lime (B. 24, 306); (4) by heating o-diamidodiphenyl with acids (B. 25, 133); (5) from o-amidodiphenylamine through the diazo-compound. The phenylazimidobenzene, produced at first, yields, when exposed to a higher temperature, nitrogen and carbazole (A. 291, 16):



Behavior: Carbazole gives the *pine-shaving reaction* (p. 457) and the blue coloration with sulphuric acid and isatin (p. 453), just the same as the pyrrol and most of the indol derivatives. This and its other deportments would justify the conclusion that it is dibenzopyrrol or benzoïndol—*e. g.*, tetrahydrocarbazole, when fused with potassium hydroxide, breaks down into α-indol carboxylic acid:



Carbazole, like pyrrol, is a very feeble base. It forms a stable salt with picric acid; the *picrate* melts at 182°. Nitrous acid converts it into *nitrosocarbazole*, $(C_6H_4)_2N.NO$, melting at 84°. Heated with potash it yields *carbazole-potassium*, $(C_6H_4)_2NK$. Alkyl iodides convert this into **n-methyl carbazole**, $(C_6H_4)N.CH_3$, melting at 87°, and **n-ethyl carbazole**, $(C_6H_4)_2N.C_2H_5$, melting at 68°. Carbazole and acetic anhydride yield n-*acetyl carbazole*, $(C_6H_4)_2N.COCH_3$, melting at 69°. Chlorine produces various *chlorcarbazoles*, nitric acid, *nitrocarbazoles* (A. 202, 27; B. 29, R. 292, 650, 1112). See p. 338 for **diamidocarbazole**. When carbazol and oxalic acid are fused together **Tricarbazole Carbinol** or **Carbazole Blue** (compare p. 358) results. **Dimethyl Carbazole,** *Ditolylimide*, $(CH_3.C_6H_3)_2NH$, melting at 364°, is made from o-toluidine by the pyrogenic method (B. 29, 2594).

Hydrocarbazoles: **Tetrahydrocarbazole,** $C_6H_4{<}\genfrac{}{}{0pt}{}{}{NH}{>}C_6H_8$, melting at 119°, results from the reduction of carbazole, as well as from the phenylhydrazone of ketohexamethylene, analogously to Fischer's indol synthesis (p. 296). It behaves like an alkylic indol (compare hydronaphthalenes, p. 466). When acted upon by alkyl iodides or with chloroform, it passes in a similar manner into acridine derivatives, just as the indols become quinoline compounds (Gaz. chim. ital. 24, 111). By the potash fusion it, like

the alkylic indols, yields indol carboxylic acid (see above and B. **26**, 2006). **Tetrahydrocarbazole Carboxylic Acid,** $C_6H_4\langle{}_{NH}\rangle C_6N_7 . COOH$, melting at 230°, is formed from the phenylhydrazone of ketohexahydrobenzoic acid (p. 301) (B. **22**, 2185). **Hexahydrocarbazole,** $C_6H_4\langle{}_{NH}\rangle C_6H_{10}$, melting at 99° and boiling at 267°, is a strong base (A. **163**, 352), just like the pyrrol and indol hydrides (pp. 461, 470).

The following are similar to carbazole in method of production and in their behavior: **Phenylnaphthyl-carbazole** or **Naphthophenocarbazole,** $C_6H_4\langle{}_{NH}\rangle C_{10}H_6$ (B. **27**, 3066), melting at 330°, occurs in coal-tar (B. **12**, 2242). An isomeric **naphthophenocarbazole,** melting at 120°, is obtained by a zinc-dust distillation from its *carboxylic acid*, $C_6H_4 . NH . C_{10}H_5 . COOH$, melting at 335°, which results from the indol condensation of phenylhydrazine with 2,3-oxynaphthoic acid (p. 408). **Dinaphthyl-carbazole** or **Dinaphtho-carbazole,** $C_{10}H_6\langle{}_{NH}\rangle C_{10}H_6$; the *a-body* melts at 216°, and the *β*-compound at 170° (B. **19**, 2242).

B. POLYHETEROATOMIC FIVE-MEMBERED RINGS.

The acetals and mercaptals of ethylene glycol—*e. g.*, ethylene-ethidene ether, $\begin{matrix} CH_2 - O \\ | \\ CH_2 - O \end{matrix}\!\!>CH . CH_3$, and *ethylene dithioethidene*, $\begin{matrix} CH_2 - S \\ | \\ CH_2 - S \end{matrix}\!\!>CH . CH_3$ (1, 298, 305)—are five-membered rings with two O- or S-atoms. This is also the case with the ethylene esters of the carbonic acid group—*e. g.*, *carbonic ethidene ester*, $\begin{matrix} CH_2 - O \\ | \\ CH_2 - O \end{matrix}\!\!>CO$, and *trithiocarbonic ethylene ester*, $\begin{matrix} CH_2 - S \\ | \\ CH_2 - S \end{matrix}\!\!>CS$ (1, 392), the ethidene esters of *a*-oxyacids—*e. g.*, *lactic ethidene ester*, $\begin{matrix} CH_3 - CH - O \\ | \\ OC \text{———} O \end{matrix}\!\!>CH . CH_3$, and *chloralide*, its chlorination product (1, 340).

Several five-membered cyclic esters and amido-derivatives have also been obtained from phosphoric acid—*e. g.*, the *lactone* of *benzoylphenylhydrazido-phosphoric acid*, $\begin{matrix} N - N(C_6H_5) \\ \| \\ C_6H_5 . C - O \text{———} \end{matrix}\!\!>POOH$, which results on treating the reaction product of PCl_5 and benzoylphenylhydrazine with methyl alcohol. o-Toluylene diamine and PCl_5 or PCl_3 yield compounds like $C_7H_6<{}^{NH}_{NH}>PO . NH . C_7H_6 . NH_2$.

AZOLES.

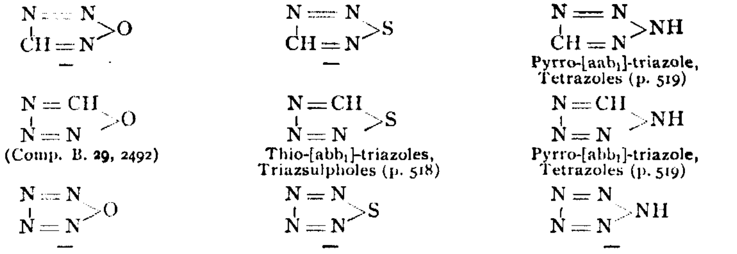
There is another group, of greater importance than those discussed. It comprises the bodies containing polyheteroatomic five-membered rings, which are embraced under the name *azoles* (A. **249**, 1; B. **24**, 2824; B. **22**, R. 737). They contain as hetero-atoms N and O, N and S, or only N-atoms. We may view them as derived from the monohetero-atomic rings—furfurane, thiophene, and pyrrol—by the replacement of methine-groups by N-atoms, whereby, as previously indicated, the stability of the ring is very slightly affected. Viewing the numerous classes of bodies

belonging here as ring-azo-substitution products of the monohetero-atomic rings, we arrive at a natural systemization of the former, and also reach a simple nomenclature for them, which in many instances is quite similar to the names which have become peculiar to the individual groups. The individual azoles, depending upon whether they are derived from furfurane, thiophene, or pyrrol, by the replacement of one, two, or three CH-groups by N-atoms, are designated as furo-monazoles, thio-diazoles, pyrro-triazoles. To distinguish the metameric rings the methine groups of furfurane, etc., are termed

$$[a], [a_1], [b], [b_1] \quad \begin{array}{l}[b]CH = CH[a]\\ \quad | \\ [b_1]CH = CH[a_1]\end{array} > R,$$

and the substituents as α, α_1, β, β_1 (p. 447), so that we distinguish *furo*-[a]-*monazole*, *furo*-[b]-*monazole*, *pyrro*-[aa$_1$]-*diazole*, *pyrro*-[ab]-*diazole*, *pyrro*-[ab$_1$]-*diazole*, etc. Retaining the names of the individual bodies and the groups introduced by their discoverers, there will in the following page be placed at the beginning of each individual group the names resulting from the introduction of the nomenclature just described. This will render the constitution and the position of the azoles in the system, which follows, very evident:

$\begin{array}{l}CH = CH\\ CH = CH\end{array} > O$ Furfurane	$\begin{array}{l}CH = CH\\ CH = CH\end{array} > S$ Thiophene	$\begin{array}{l}CH = CH\\ CH = CH\end{array} > NH$ Pyrrol
$\begin{array}{l}CH = N\\ CH = CH\end{array} > O$ **Furo-[a]-monazole, Isoxazole (p. 493)**	$\begin{array}{l}CH = N\\ CH = CH\end{array} > S$ Thio-[a]-monazole, Comp. Benzisothiazole (p. 507)	$\begin{array}{l}CH = N\\ CH = CH\end{array} > NH$ Pyrro-[a]-monazole, Pyrazole (p. 480)
$\begin{array}{l}N = CH\\ CH = CH\end{array} > O$ Furo-[b]-monazole, Oxazoles (p. 502)	$\begin{array}{l}N = CH\\ CH = CH\end{array} > S$ Thio-[b]-monazole, Thiazoles (p. 504)	$\begin{array}{l}N = CH\\ CH = CH\end{array} > NH$ Pyrro-[b]-monazole, Imidazoles, Glyoxalines (p. 496)
$\begin{array}{l}CH = N\\ CH = N\end{array} > O$ Furo-[aa$_1$]-diazole, Furazanes (p. 514)	$\begin{array}{l}CH = N\\ CH = N\end{array} > S$ Thio-[aa$_1$]-diazoles, Piazthioles (p. 518)	$\begin{array}{l}CH = N\\ CH = N\end{array} > NH$ Pyrro-[aa$_1$]-diazole, Osotriazole (p. 508)
$\begin{array}{l}N = N\\ CH = CH\end{array} > O$ **Furo-[ab]-diazole, Anhydrides of o-Diazophenols (p. 516)**	$\begin{array}{l}N = N\\ CH = CH\end{array} > S$ **Thio-[ab]-diazole, Anilidothiobiazole, Phenylenediazosulphides (p. 517)**	$\begin{array}{l}N = N\\ CH = CH\end{array} > NH$ **Pyrro-[ab]-diazole (p. 510)**
$\begin{array}{l}N = CH\\ N = CH\end{array} > O$ **Furo-[bb$_1$]-diazole, Oxybiazoles (p. 516)**	$\begin{array}{l}N = CH\\ N = CH\end{array} > S$ **Thio-[bb$_1$]-diazole, Thiobiazolines (p. 517)**	$\begin{array}{l}N = CH\\ N = CH\end{array} > NH$ **Pyrro-[bb$_1$]-diazole (p. 511)**
$\begin{array}{l}N = CH\\ CH = N\end{array} > O$ **Furo-[ab$_1$]-diazole, Azoximes (p. 515)**	$\begin{array}{l}N = CH\\ CH = N\end{array} > S$ **Thio-[ab$_1$]-diazole, Azosulphimes (p. 517)**	$\begin{array}{l}N = CH\\ CH = N\end{array} > NH$ **Pyrro-[ab$_1$]-diazole, Triazoles (p. 511)**



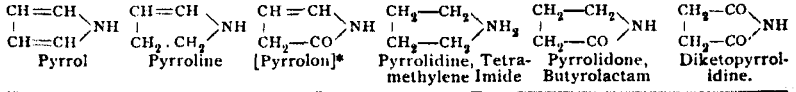
The parent substances of all the rings just given have not been prepared. In most instances, however, their next homologues are known; in some cases only the *benzo*-derivatives. Only single representatives of the furo- and thiotriazoles are known at the present time. It is, however, not impossible that by synthesis these rings, consisting mainly of inorganic elements, may be multiplied and the system enlarged. Indeed, we may succeed to such a degree that the purely inorganic rings—*e. g.*, those constructed from four N-atoms and an NH group—will be prepared. This would be a ring homologue of hydrazoic acid. From the standpoint of a *nitrogen chemistry* the C-containing rings could be as readily evolved from the nitrogen ring by replacing the N-atoms with CH-groups, as was suggested above in the reverse case.

The numerous and important *pyrazoles*, together with their benzo-derivatives, the *indazoles*, consisting of dihetero-atomic rings, will be next discussed; then will follow the *isoxazoles*, with their *benzo*-derivatives, the *indoxazenes*. After this will appear the glyoxalines or *imidazoles*, the *oxazoles*, and the *thiazoles*, sometimes in conjunction with their benzo-derivatives, which it is customary to consider under the name of *anhydro-bases* (pp. 95, 153, 157), because they are formed from o-diamines, o-amidophenols, and o-amidothiophenols with carboxylic acids by the exit of water. In the trihetero-atomic rings, again, the groups of the pyrrodiazoles or *triazoles* are placed first; the *azimides* and *pseudoazimides* belong to their benzo-derivatives. Attached to these are the furodiazoles: the *furazanes*, *diazo-oxides*, *oxybiazoles*, *azoximes*; and the *thiodiazoles*: *azosulfimes*, *thiobiazolines*, *piazthioles* (*piaselenols*), *thio*-[ab]-*diazoles*, and *phenylenediazosulphides*. The *triazsulpholes* and *tetrazoles* conclude the list.

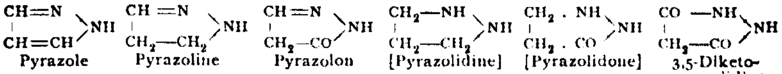
1. PYRAZOLE- OR PYRRO-[a]-MONAZOLE GROUP.

Pyrazole, $C_3H_4N_2$, may be regarded as derived from pyrrol by replacement of a methine-group adjacent to an NH-group by nitrogen—*pyrro*-[a]-*monazole* (see above). See 3-methylpyrazole (p. 482) for details in regard to the constitution of pyrazole. There are a *dihydropyrazole* or *pyrazoline* and a *tetrahydropyrazole* or *pyrazolidine* corresponding to the di- and tetrahydropyrrols.

Keto-substitution products of these hydrogenized pyrazoles are keto-pyrazoline or *pyrazolon*, among the derivatives of which is the febrifuge *antipyrine*, ketopyrazolidine or *pyrazolidone*, and *diketopyrazolidine*, corresponding to the butyrolactam or pyrrolidone (p. 462) and succinimide. The subjoined diagram indicates the relations existing between these pyrazole and the pyrrol derivatives:



* The parent substances, enclosed in brackets, are only known in their derivatives.



Pyrazole — Pyrazoline — Pyrazolon — [Pyrazolidine] — [Pyrazolidone] — 3,5-Diketo-pyrazolidine.

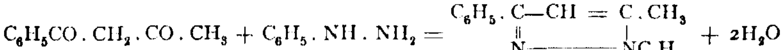
Pyrazole, $C_3H_4N_2$, melting at 70° and boiling at 187°, results from epichlorhydrin, hydrazine hydrate, and zinc chloride (B. 23, 1105). A better method consists in splitting off CO_2 from its carboxylic acids (B. 26, R. 282), or in the action of bromine upon pyrazoline (p. 486) (B. 29, 775). It is a feeble base; its salts are unstable. It does not combine with methyl iodide. An ammoniacal silver solution precipitates *pyrazole silver*, $C_3H_3H_2Ag$, corresponding to pyrrol-potassium (p. 458). The *platinum double salt*, $(C_3H_4N_2 . HCl)_2PtCl_4$, at 200–210°, loses four molecules of hydrochloric acid and becomes $(C_3H_3N_2)_2PtCl_2$ (B. 26, R. 185). n-*Acetyl pyrazole*, boiling at 156°, and n-*benzoyl pyrazole*, boiling at 281°, result from the action of acetyl chloride and benzoyl chloride upon pyrazole (B. 28, 716).

The pyrazole derivatives are designated in the following manner:

$\begin{matrix} 3\,CH = N_2 \\ 4\,CH = CH_5 \end{matrix} > NH\ 1$ (or n); the numbering proceeds from the imide group, beyond the second nitrogen atom.

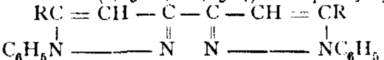
1. **Homologous Pyrazoles** are formed:

1. From the hydrazones of the β-diketones and β ketone aldehydes or oxymethylene ketones. As a rule, the reactions proceed smoothly with the elimination of water, when the ketones are digested with the hydrazines:



Benzoyl Acetone — 1,3,5-Diphenylmethyl Pyrazole.

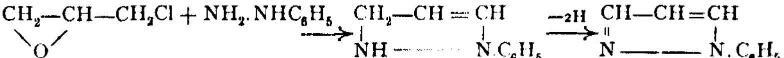
By this procedure the unsymmetrical β-diketo-compounds yield two isomeric pyrazoles; this is because the two possible hydrazones are formed. In the example cited the 1,5,3-*body* is produced, together with 1,3,5-diphenylmethyl pyrazole. The oxalyldiketones (I, 521; II, 514) and phenylhydrazine yield the *bisphenylalkyl pyrazoles*:



(A. 278, 295).

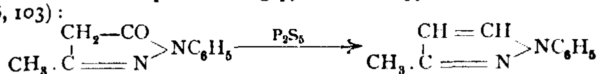
2. By the elimination of carbon dioxide from the homologous pyrazole carboxylic acids (p. 484).

3. By the exit of hydrogen from the pyrazolines (p. 485). Frequently, in reactions where pyrazolines may well be expected pyrazoles appear. This is true of the interaction of the hydrazines and epichlorhydrin:



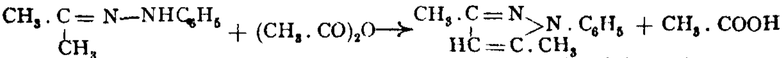
Epichlorhydrin — (n-Phenylpyrazoline) — n-Phenylpyrazole.

4. Pyrazoles also result upon distilling pyrazolons or pyrazolidones with zinc-dust or P_2S_5 (B. 26, 103):



Phenylmethylpyrazolon — Phenylmethylpyrazole.

5. Certain hydrazones of mono-ketones yield pyrazoles when they are heated with acid anhydrides (Bull. Soc. Chim. [3], 11, 115; see B. 28, 703 Anm. 4):



Acetophenylhydrazone — 1,3,5-Phenyldimethylpyrazole.

Behavior: The homologous pyrazoles may be arranged in three groups: (1) pyrazoles with free imide-group; (2) n-alkyl substituted pyrazoles, which can be obtained from

the first class (or their silver salts) by the action of alkyl iodides—best by the distillation of the iod-alkylates (B. **28**, 716) with an excess of alkyl iodide—or from β-diketones and alkylhydrazines; (3) n-phenyl substituted pyrazoles, which are made through the phenylhydrazines, and are chiefly distinguished by their stability and power of crystallization.

All pyrazole homologues are feeble bases. They form double salts with silver nitrate, mercuric chloride, and platinic chloride. The platinum double salts, like pyrazole itself, part with 4 HCl on heating and become R_2PtCl_2 (R = the pyrazole residue). They usually combine with alkyl iodide to form ammonium compounds (see above).

Potassium permanganate oxidizes the c-alkylized pyrazoles to pyrazole carboxylic acids, in contradistinction to the pyrrols, which are burnt up by this reagent (B. **22**, 172).

In the n-phenylated pyrazoles during the oxidation the phenyl group is often split off and replaced by hydrogen. This is particularly true if it be amidated. The behavior is quite different during *reduction*. Pyrazoles with the free imide-group are but slightly altered by the reducing agents (A. **273**, 266). n-Phenylpyrazoles are reduced to pyrazolines (p. 485), which yield intense colorations with ferric chloride, chromates, etc. (*Knorr's pyrazoline reaction*). In more energetic reductions *trimethylene diamine derivatives* are formed by the rupture of the union between the N-members. In some n-phenylpyrazoles the reduction is accompanied by the splitting-off of the phenyl group as benzene or some similar group.

(1) *Pyrazoles with free imide hydrogen*: 3- (or 5-) **Methyl Pyrazole**,

$$C_4H_6N_2 = \begin{array}{l} CH_3.C - \overset{H}{N} - N \\ \quad\;\; | \qquad\qquad\; | \\ \quad\; CH - - - CH \end{array}$$

(see below), is an oil, boiling at 204°. It results

(1) from the interaction of oxymethylene acetone and hydrazine;
(2) from its carboxylic acids;
(3) as well from 1,3- as from 1,5-phenylmethylpyrazole by elimination of the phenyl group through oxidation (A. **279**, 217–225).

The last two methods show conclusively that 3-methyl pyrazole and 5-methyl pyrazole are identical. It is concluded, therefore, that pyrazole, like benzene, possesses "oscillating linkages"; the imide hydrogen atom is capable of oscillating between the two N-atoms (Knorr, A. **279**, 188). The formula presented above for pyrazole is supposed to represent this condition.

3,5 **Dimethyl Pyrazole**, $\overline{NH - N = C(CH_3) - CH = C(CH_3)}$, melts at 107° and boils at 220°. It is obtained from acetyl acetone and hydrazine, and from 1,3,5-phenyldimethyl pyrazole by reduction (*elimination of the* C_6H_5*-group*) (B. **25**, R. 163, 744).

3,4,5-**Trimethyl Pyrazole**, $\overline{NH - N = C(CH_3) - C(CH_3) = C(CH_3)}$, melting at 138° and boiling at 233°, is obtained from methylacetyl acetone. 3,4,4,5-**Tetramethyl Pyrazole**, $\overline{N = C(CH_3) - C(CH_3)_2 - C(CH_3) = N}$, melting at 50–55°, and boiling at 243°, is formed from dimethylacetyl acetone (A. **279**, 244, 247). 3- (or 5-) **Phenylpyrazole**, $\begin{array}{l} C_6H_5C - \overset{H}{N} - N \\ \quad\;\; | \qquad\qquad\; | \\ \quad\; CH - - - CH \end{array}$, melting at 78°, is formed from benzoyl acetaldehyde (p. 250) (B. **28**, 696).

Isomeric 4-**Phenyl Pyrazole**, melting at 228°, is obtained from 1,4-phenyl pyrazole carboxylic acid (A. **279**, 254; B. **27**, 3247; **28**, 223, 699). 3,5-**Phenyl Methyl Pyrazole**, $\overline{NH - N = C(CH_3) - CH = C(C_6H_5)}$, melting at 128° and boiling at 317°, has been prepared from benzoyl acetone (A. **279**, 248), as well as from phenylmethylisoxazole (p. 494), on heating with alcoholic ammonia (B. **28**, 2952).

(2) n-*Alkyl Pyrazoles*: n- (or 1-) **Methyl Pyrazole**, $C_3H_3N_2.CH_3$, boiling at 127°, is formed in the interaction of pyrazole silver and methyl iodide (B. **26**, R. 281; **28**, 716). 1,3-**Dimethyl Pyrazole**, $C_3H_2(CH_3)N_2.CH_3$, boils at 150° (A. **279**, 231); 1,3,5-**Trimethyl Pyrazole**, $C_3H(CH_3)_2N_2CH_3$, melting at 37° and boiling at 170°, **crystallizes in combination with one molecule of chloroform.** 1,3,4,5-**Tetramethyl**

Pyrazole, $C_3(CH_3)_3N_2CH_3$, boils at 190–193°. These compounds are also formed from acetyl acetone and methylacetyl acetone by the action of methylhydrazine (A. **279**, 232, 235).

(3) n-*Phenyl Pyrazoles*: n- (or 1-) **Phenyl Pyrazole**, $C_3H_3N_2 . C_6H_5$, melting at 11° and boiling at 246°, with sp. gr. 1.1125, is obtained from epichlorhydrin and phenylhydrazine (see above), as well as from its carboxylic acids. It yields, upon reduction, phenylpyrazoline together with trimethylenephenyldiamine. n-**Tolylpyrazole**, $C_3H_3N_2 . C_7H_7$, melting at 33° and boiling at 259°, yields in like manner trimethylenetolyldiamine (Gaz. ch. ital. **18**, 354). 1-**Phenyl-3-methyl Pyrazole** melts at 37° and boils at 255°. Its *iodmethylate* melts at 144°. The first body is derived from phenylmethylpyrazolon (p. 481, A. **238**, 203; B. **24**, 648), as well as from oxymethylene acetone together with the isomeric 1-**Phenyl-5-methyl Pyrazole**,

$C_6H_5N - N = CH - CH = C(CH_3)$ (ring closed between N and C). This is an oil, boiling at 255°. Its *iodmethylate* melts with decomposition at 296°. 1-**Phenyl-4-methyl Pyrazole**,

$C_6H_5N - N = CH - C(CH_3) = CH$ (ring closed between N and CH), boiling at 266°, is formed by a rearrangement of the iodmethylate of 1-phenyl pyrazole (B. **26**, R. 327). 1-**Phenyl-3,5-dimethyl Pyrazole**, $C_3(CH_3)_2HN_2 . C_6H_5$, boiling at 273°, is obtained from acetyl acetone. Upon reduction it yields dimethyl pyrazole and benzene, together with 1-*Tetrahydrophenyl-3,5-dimethyl pyrazole*, which, by oxidation, is decomposed into dimethyl pyrazole and adipic acid (B. **26**, R. 246). 1-**Phenyl-3,4-dimethyl Pyrazole**, boiling at 278°, results from oxymethylene methylethyl ketone, $CHOH = C(CH_3) - CO . CH_3$ (B. **25**, R. 943). 1,3-**Diphenyl Pyrazole**, $C_3H_2(C_6H_5)N_2 . C_6H_5$, melting at 56° and boiling at 337°, is obtained from benzoylacetaldehyde (B. **21**, 1135); 1,5-**Diphenyl Pyrazole**, melting at 54° and boiling at 340°, is derived from its carboxylic acid (B. **25**, 3145); 1,3,5-**Triphenyl Pyrazole**, $C_3H(C_6H_5)_2 . N_2 . C_6H_5$, melting at 212°, is made from its carboxylic acid (B. **26**, 1881). See A. **289**, 332, for the production of 1,3,4-**triphenyl pyrazole**, melting at 185°, by the decomposition of 1,3,4,6 **tetraphenyldihydropyridazine**.

2. **Haloid-, nitro-, amido-pyrazoles, pyrazole-sulphonic acids.**—The halogens replace the hydrogen atoms in pyrazole. Bromine reacts most readily. The halogen atoms in the 4-position are most securely combined. In the sulphonation and nitration of pyrazole the NO_2 and SO_3H-groups also enter the nucleus. n-Phenylated pyrazoles are nitrated and sulphonated in the phenyl residue. n-Sulphophenyl-pyrazole-acids have also been prepared by the introduction of phenylhydrazine-sulphonic acids in the pyrazole syntheses (A. **278**, 296). In the nitropyrazoles the basic character of the pyrazoles disappears. They are acids, which form stable sodium, potassium, etc., salts.

The amido-pyrazoles result in the reduction of the corresponding nitro-bodies. They resemble the aromatic amines in their deportment. They have also been obtained by the action of hydrazines upon the nitriles of β-ketone-carboxylic acids and upon malononitrile.

4-**Brom-pyrazole**, $C_3H_3BrN_2$, melts at 97°. 3-**Methyl-brom-pyrazole** melts at 67° (A. **279**, 227). 1,3,5-**Triphenyl-brom-pyrazole** melts at 142°. 1-**Phenyl-tribrom-pyrazole** melts at 107°. **Iod-pyrazole** melts at 108° (B. **26**, R. 281). 4-**Nitro-pyrazole**, $C_3H_3(NO_2)N_2$, melts at 142°. 3-**Methyl-4-nitro-pyrazole**, melting at 134° and boiling at 325°, is made by nitrating methyl-pyrazole or 3-methyl-5-pyrazole carboxylic acid with a mixture of nitric and sulphuric acids (A. **279**, 228). 4-**Nitro-1,3,5-trimethyl-pyrazole**, melting at 57°, yields upon reduction:

4-**Amido-1,3,5-trimethyl-pyrazole**, melting at 103°, which may be readily converted into diazo-compounds, and subsequently, by combination with anilines, phenols, etc., into azo-dyes. 1-**Phenyl-3,4-ethylmethyl-5-amido-pyrazole**, melting at 81°, is prepared from methyl propionyl-acetonitrile, $C_2H_5COCH(CH_3)CN$, and phenylhydrazine (Bull. Soc. Ch. [4], **4**, 647). 3,5-**Diamido-pyrazole**, $C_3(NH_2)_2H_2N_2$ (?), is formed from malononitrile and hydrazine acetate (B. **27**, 690).

Methyl-pyrazole-sulphonic Acid, $C_3H_2N_2(CH_3)(SO_3H)$, melting at 258°, is formed when fuming sulphuric acid acts upon methyl-pyrazole (A. **279**, 230).

3. **Oxypyrazoles**: In certain reactions the pyrazolons (p. 486) behave as such. In alkylizing, these yield alkoxypyrazoles, together with isomeric n-alkyl derivatives (antipyrines). Further, compounds are also formed in the interaction of acid haloids and

pyrazolons, which are probably to be viewed as esters of oxypyrazoles. The alkyl iodides and alkoxypyrazoles yield addition products, which also result from the antipyrines and alkyl iodides, and when they are gently heated, alone or with alkali, they are reconverted into antipyrines. The acid esters of the oxypyrazoles also yield alkyl iodide addition products, which may be resolved into antipyrines (J. pr. Ch. [2], **54**, 177; **55**, 145; A. **293**, 42). Alkoxypyrazoles are also produced by the elimination of water from the hydrazones of the β-ketonic esters by means of suitable reagents.

n-Phenyl-5-ethoxy-pyrazole, $C_6H_5N.N:CH.CH:C(OC_2H_5)$, is formed from its carboxylic ester, which is produced by the condensing action of zinc chloride upon the phenylhydrazone of oxalacetic ester, then saponifying and splitting off carbon dioxide (B. **26**, R. 550).

When the ethoxy-group is saponified with hydrochloric acid n-phenlypyrazolon, melting at 118° (p. 488; B. **27**, 407), results. **n-Phenyl-3-methyl-5-methoxypyrazole,** $C_6H_5N.N:C(CH_3).CH:C(OCH_3)$, boiling at 240°, is formed when diazomethane acts upon phenyl-methyl-pyrazolon (B. **28**, 1626), or methyl iodide and sodium methylate, together with the isomeric antipyrine (p. 488); also by the action of phenylhydrazine and hydrochloric acid upon the methyl ester of acetoacetic acid. Its **iodmethylate,** which is also produced from antipyrine and methyl iodide, readily changes to antipyrine on boiling with sodium hydroxide (p. 488 and A. **293**, 17). **n-Phenyl-3-methyl-5-ethoxypyrazole,** melting at 38° and boiling at 301°, is formed from the phenylhydrazone of acetoacetic ester by means of acetyl chloride or an excess of hydrochloric acid. It yields phenylmethylpyrazolon when it is saponified. Sodium and alcohol convert it into phenylmethylpyrazoline (B. **28**, 627, 635, 706). The last two esters have also been obtained, by carbon dioxide elimination, from **carbomethoxy-** and **carboethoxy-phenylmethylpyrazolons,** products resulting from the action of chlorcarbonic methyl and ethyl esters upon phenylmethylpyrazolon (see above, and J. pr. Ch. [2], **54**, 180; **55**, 140).

4. **Pyrazole Ketones** are produced, like the thiophene, pyrrol, and indol ketones, on heating the pyrazoles with acid chlorides:

1-Phenyl 4-acetyl-pyrazole, $C_3(COCH_3)H_2N_2.C_6H_5$, melting at 122°. Its *oxime* melts at 130° and its *phenylhydrazone* at 143° with decomposition. **1-Phenylbenzoyl-pyrazole,** $C_3(COC_6H_5)H_2N_2C_6H_5$, melts at 123°; its *oxime* at 143° and its *phenylhydrazone* at 139° with decomposition.

5. **Pyrazole Carboxylic Acids** are produced

1. By oxidizing alkyl pyrazoles with potassium permanganate. When several alkyl groups are present they are gradually changed to carboxyl.

2. Pyrazole carboxylic esters are formed synthetically by the action of hydrazines upon the carboxylic esters of β-diketones or oxymethylene ketones:

$$C_6H_5CO.CH_2.CO.CO_2R + NH_2.NHC_6H_5 \longrightarrow C_6H_5N{-}N=C(C_6H_5){-}CH=C.CO_2R$$

Acetophenone Oxalic Ester — 1,3-Diphenyl-5-pyrazole Carboxylic Ester.

The γ-diketonic esters also, which result from the interaction of bromacetone, bromacetophenone, etc., with sodium acetoacetic ester, yield, by action of diazobenzene salts with the splitting-off of the acetyl group, phenylhydrazones of β-diketone carboxylic esters, which condense to pyrazole carboxylic esters (B. **26**, 1881).

3. Pyrazole carboxylic esters are formed by the addition of diazoacetic esters to mono- and dicarboxylic acids of the acetylene series (B. **22**, 2165; A. **273**, 222):

Diazoacetic Ester — **Acetylene Dicarboxylic Ester** — **3,4,5-Pyrazole Tricarboxylic Ester.**

Monohalogen substitution products of the acrylic and fumaric series and α,β-dihaloid substituted saturated acids—*e. g.*, α,β-dibrompropionic acid, dibromsuccinic acid, etc.—react with diazoacetic ester. When the pyrazole carboxylic acids are heated carbon dioxide is evolved and pyrazole results. The carboxyl group in the 3-position is most easily split off. The next in order is that in the 5-position, while the COOH-group in the 4-position is most firmly combined (A. **278**, 273). There is no N atom adjacent to it.

3- (or 5-) **Pyrazole Carboxylic Acid,** $C_3H_3N_2 . COOH$, melting at 209° with decomposition, is obtained from 3-methyl pyrazole (p. 482), as well as from 3,5-pyrazoline dicarboxylic acid by the exit of carbon dioxide and H_2 (A. **273**, 237). 4-**Pyrazole Carboxylic Acid,** melting at 275°, is obtained from pyrazole tricarboxylic acid. **3,5-Pyrazole Dicarboxylic Acid,** $C_3H_2N_2(COOH)_2$, melting at 289°, is made from methyl pyrazole carboxylic acid, dimethyl pyrazole (A. **279**, 218; B. **25**, R. 744), as well as from diazoacetic ester by means of dibrompropionic ester. **3,4,5-Pyrazole Tricarboxylic Acid,** $C_3HN_2(COOH)_3$, melting at 233°, is prepared by methods 1 and 3 (p. 484).

3-**Methyl-5-pyrazole Carboxylic Acid,** $C_3H_2(CH_3)N_2 . COOH$, melts at 236° (B. **25**, R. 744; A. **279**, 217). **3,5-Dimethyl-4-pyrazole Carboxylic Acid,** $C_3H(CH_3)_2N_2 . COOH$, melting with decomposition at 290°, is derived from acetyl- or ethidene-acetoacetic ester (A. **279**, 239). Two isomeric c **Phenylpyrazole Dicarboxylic Acids,** $C_3(C_6H_5)HN_2(CO_2H)_2$, melting at 235° and 243°, have been obtained from diazoacetic ester by means of phenylpropiol- and α-bromcinnamic acid (B. **27**, 3247). n-**Phenylpyrazole Carboxylic Acid,** $C_3H_2N_2(C_6H_5)COOH$; the 3-*acid* melts at 146°, and the 5-*acid* melts at 183° (B. **24**, 1888). The 4-*acid* melts at 220°. It is obtained from n-phenylpyrazole tricarboxylic acid (B. **22**, 179). n-**Phenylmethylpyrazole Carboxylic Acids,** $C_3H(CH_3)N_2 . C_6H_5(COOH)$. There are five known isomerides: (1) the 1,5,3-*acid*, melting at 136°, results from the action of diazobenzene chloride upon acetonyl acetoacetic ester (p. 484, method 2), as well as from acetone oxalic ester and phenylhydrazine, together with (2) the 1,3,5-*acid*, melting at 190°, which is also produced by a peculiar rearrangement of phenylmethyloxypyridazone (see this) (A. **253**, 54; **295**, 305); (3) the 1,5,4-*acid*, melting at 166°, is obtained from oxymethylene acetoacetic ester (A. **278**, 270; **295**, 311); (4) the 1,4,3-*acid*, melting at 134°, and (5) the 1,3,4-*acid*, melting at 192°, have been prepared by a half-sided oxidation of phenyldimethylpyrazole (B. **25**, R. 943; **26**, R. 245). **1,5-Diphenyl-3-pyrazole Carboxylic Acid,** $C_3H(C_6H_5)N_2 . C_6H_5 COOH$), melting at 185°, is prepared from phenacylacetoacetic ester; **phenylpyrazole dicarboxylic acids**—compare A. **295**, 306. **1-Phenyl-3,4,5-tricarboxylic Acid,** $C_3N_2 . C_6H_5(COOH)_3$, melts at 184° (B. **22**, 172).

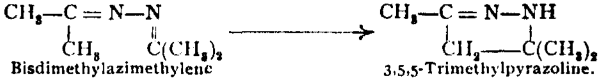
PYRAZOLINES.

Metallic sodium and alcohol reduce the pyrazoles, especially the n-phenylpyrazoles, to dihydropyrazoles or pyrazolines. The latter are also produced by rearrangement of the hydrazones of unsaturated aldehydes or ketones, in that the amine residue of the hydrazine adds itself to the unsaturated linkage:

Acroleïn Phenylhydrazone — n-Phenylpyrazoline.

While this rearrangement proceeds with many hydrazones at lower temperatures, with others it is only completed when they are distilled. Frequently it occurs that the corresponding pyrazole (p. 481) is formed instead of the pyrazoline, or is produced along with the latter.

The ketazine of acetone, bisdimethylazimethylene, is capable of a rearrangement similar to the preceding. It is changed quite readily by maleïc acid into maleïnate of trimethylpyrazoline:



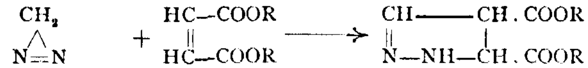
Bisdimethylazimethylene 3,5,5-Trimethylpyrazoline.

Behavior: The pyrazolines are feeble bases. They are, for the most part, only soluble in concentrated acids. They are less stable than the pyrazoles. Oxidizing agents convert them into very unstable dye-substances, which are probably derived from bis-pyrazolines (B. **26**, 100; Knorr's pyrazoline reaction). When reduced they frequently yield trimethylene diamine derivatives; this is particularly true of the n-phenylpyrazolines.

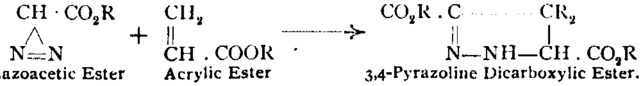
Pyrazoline, $C_3H_6N_2 = CH_2—CH_2—CH=N—NH$, is an oil, boiling at 144°. It is formed from acroleïn and hydrazine hydrate (B. **28**, 69; **29**, 774). **3,5,5-Trimethyl-pyrazoline**, $C_3H_3(CH_3)_3N_2$, boiling at 66–69° (20 mm.), is obtained from mesityl oxide and hydrazine, as well as from *bis*-dimethylazimethylene (see above); its *picrate* melts at 138° and its *maleïnate* at 127° (B. **27**, 770). **5-Phenylpyrazoline**, $C_3H_5(C_6H_5)N_2$, is obtained from the hydrazone of cinnamic aldehyde (B. **27**, 788), as well as from its dicarboxylic acid (B. **26**, 261). **n-Phenylpyrazoline**, $C_3H_5N_2 . C_6H_5$, melting at 52° and boiling at 274°, is converted by bromine into *n-phenyldibrompyrazoline*, $C_3H_3Br_2N_2 . C_6H_5$, melting at 39°.

1,3,5-Triphenyl-pyrazoline, $C_3H_3(C_6H_5)_3N_2$, melting at 135°, is changed by bromine to *triphenyltribrompyrazoline*, $C_3(C_6H_5)_3Br_3N_2$, melting at 179°.

Pyrazoline carboxylic acids are obtained from diazoacetic ester or diazomethane by means of olefine mono- and -dicarboxylic acids or mono-haloid saturated acids (compare p. 484):



Diazomethane Fumaric Ester 4,5-Pyrazoline Dicarboxylic Ester.



Diazoacetic Ester Acrylic Ester 3,4-Pyrazoline Dicarboxylic Ester.

The pyrazoline carboxylic acids show the rather remarkable peculiarity that when they are heated alone they break down into nitrogen and trimethylene carboxylic acids (p. 22). Hydrazine is split off when they are heated with hydrochloric acid. Upon oxidation they become pyrazole carboxylic acids; and when their silver salts are heated, pyrazoles are produced. Upon reduction they yield pyrazoline compounds in part (p. 490) (E. Buchner, A. **273**, 214).

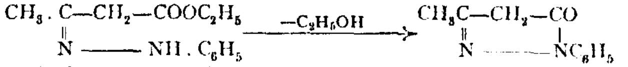
Pyrazoline-3,5-dicarboxylic Acid, $C_3H_4N_2(COOH)_2$, melts with decomposition at 242°. **Pyrazoline-4,5-dicarboxylic ester** (B. **27**, 1890), **pyrazoline-3,4,5-tricarboxylic methyl ester**, $C_3H_3N_2(COOCH_3)_3$, melting at 61°, and **pyrazoline-3,4,5,5-tricarbonacetic trimethyl ester**, $C_3H_2N_2(CO_2CH_3)_3(CH_2 . CO_2CH_3)$, melting at 105°, are obtained from diazoacetic ester by means of fumaric and aconitic esters, while **5-Phenyl-3,4-pyrazoline Dicarboxylic Methyl Ester(?)**, $C_3H_3(C_6H_5)N_2(COOCH_3)_2$, is formed from cinnamic ester and diazoacetic ester.

PYRAZOLONS.

The pyrazolons or ketodihydropyrazoles are those pyrazole derivatives which have been known for the longest time. They were discovered in 1883 and investigated by L. Knorr. Different pyrazolons have been previously discussed at the conclusion of the hydrazones of the *β*-ketonic acids, of which they are the inner anhydrides, and to which they sustain the same relation as the lactams bear to the corresponding amido-acids,

hence the designation lactazams was suggested for the pyrazolons (1, 363).

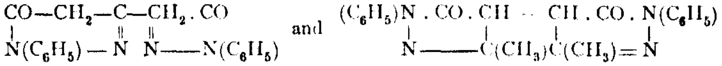
They are produced (1) by the elimination of alcohol from the hydrazones of β-ketonic esters :



Phenylhydrazone-acetoacetic Ester 1,3-Phenylmethyl-pyrazolon.

A number of these hydrazones when acted upon with condensing agents which eliminate water—*e. g.*, hydrochloric acid, acetyl chloride, etc.—yield *alkoxypyrazoles* (p. 483), which subsequently are converted by saponification of the alkoxy-group into pyrazolons. Some of the phenylhydrazones of the β-ketonic esters, when treated with concentrated sulphuric acid, yield *indol* derivatives.

When hydrazines are condensed with the esters of β,β-diketone dicarboxylic acids—*e. g.*, diaceto succinic ester and oxaldiacetic ester—bispyrazolons are produced (B. **28**, 68):



Bisphenylpyrazolon Bisphenylmethylpyrazolon.

(2) By the oxidation of the corresponding pyrazolidones.

Behavior: The pyrazolons, like the other pyrazole derivatives, are feeble bases (see, however, antipyrine). They also manifest the acid properties of the β ketonic esters, *and therefore yield unstable salts with bases just as they do with acids. They also have* a series of reactions in common with the derivatives of β ketonic acids. This is due to the reactivity of the CH_2-group standing between the two CO-groups; they condense to *benzylidene* derivatives with benzaldehyde, and with nitrous acid form *isonitroso-* or *nitroso*-compounds, while with diazobenzene salts they yield more or less intensely colored *azo*-compounds, etc. (B. **27**, 782; **28**, 625).

Different formulas have been proposed to show the constitution of the pyrazolons :

Two isomeric n-phenylpyrazoles, corresponding to the formulas I and II, have been made in various ways. Furthermore, formula II corresponds to antipyrine, the most important member of the group (p. 488). It is, however, very often quite difficult to arrive at a distinction between the different possible formulas. The alkoxypyrazoles are derived from the hydroxyl form (III) of the pyrazolons. It is true that they are also produced from pyrazolons by various alkylization methods, together with the isomeric n-alkyl derivatives constituted according to formula II (B. **28**, 706, 1626). The reaction products of acid chlorides and pyrazolons are also probably derived from the same formula (pp. 483, 484).

Pyrazolon, $\overline{CO . CH_2 . CH : N . NH}$, melting at 164°, is best prepared from formylacetic ester (1, 364) and hydrazine, but is also produced from its carboxylic acids. It condenses with benzaldehyde, nitrous acid, and diazobenzene chloride to 4-**Benzal-pyrazolon**, $(C_3H_2ON_2):CHC_6H_5$, melting at 200°, **4-isonitrosopyrazolon**, $(C_3H_2ON):NOH$, melting with decomposition at 181°, and **4-pyrazolon-azobenzene**, $(C_3H_2ON_2):N.NHC_6H_5$, melting at 196° (B. **29**, 249).

3-Methyl Pyrazolon, $C_3(CH_3)H_3ON_2$, melting at 215°, is obtained by the action of hydrazine upon acetoacetic ester or dehydracetic ester (J. pr. Ch. [2], **39**, 132).

n-Phenyl-5-pyrazolon, $\overline{CO . CH_2 . CH : N . N} . C_6H_5$, melting at 118°, is obtained both from n-phenyl-3- and 4-pyrazolon carboxylic acids and from 1-phenyl-5-pyrazoli-

done. **n-Phenyl-3-pyrazolon**, $\overline{CH : CH . CO . NH . NC_6H_5}$, melting at 154°, results upon oxidizing 1-phenyl-3-pyrazolidone with ferric chloride, and by treating n-phenyl-pyrazoline successively with bromine and caustic potash, etc. (B. **28**, 35, 630; **29**, 519; J. pr. Ch. [2], **52**, 138).

n-Phenyl-3-methyl Pyrazolon, $\overline{CO . CH_2 . C(CH_3) : N . NC_6H_5}$, melting at 127°, from acetoacetic ester, the β-chlorcrotonic esters (B. **29**, 1654), or tetrolic acid by means of phenylhydrazine, is that pyrazole derivative which is the best known, and indeed has been known for the longest time (A. **238**, 147). With benzaldehyde it yields the *benzylidene* compound, $\overline{CO . C(: CHC_6H_5)C(CH_3) : N . N} . C_6H_5$, melting at 107°; with N_2O_3 an *isonitroso*-derivative, $\overline{CO . C(NOH)C(CH_3) : N . NC_6H_5}$, melting at 157°, which may be oxidized and reduced to *nitro-* and *amido-phenylmethyl pyrazolon*. The latter is also made by the reduction of *phenylmethyl pyrazolon azobenzene*. When the amido-derivative is oxidized it becomes *rubazonic acid*, $C_{20}H_{17}N_5O_2$, melting at 181°. It is a red-colored compound, which in its behavior recalls the purpuric acid (1, 510) of the uric acid group. A large excess of the oxidant converts amidopyrazolon immediately into **4-Keto-1-phenyl-3-methyl-pyrazolon**, $\overline{CO . CO . C(CH_3) : N . NC_6H_5}$, the isatin of the pyrazole group, which, by reduction, yields the corresponding secondary alcohol: **4-Oxy-1-phenyl-3-methyl pyrazolon** (A. **293**, 50).

Ferric chloride oxidizes phenylmethyl pyrazolon, with the union of two molecules, to *Pyrazole Blue*, $\begin{array}{l} C_6H_5N—CO—C=\!=\!=C—CO—NC_6H_5 \\ \;\;\;\; N=\!=\!=CCH_3 \;\; CH_3C=\!=\!=N \end{array}$, which resembles indigo-blue in constitution and chemical behavior. Less energetic oxidants—*e. g.*, phenylhydrazine, etc.—produce *bisphenylmethylpyrazolon*, which contains two atoms more of hydrogen. This can also be prepared from phenylmethylpyrazolon silver and iodine, as well as from the diphenylhydrazone of diacetosuccinic ester (p. 473). The interaction of diazomethane and phenylmethyl pyrazolon yields phenylmethylmethoxypyrazole (p. 487), and along with it, but in small quantity, the isomeric antipyrine (compare B. **28**, 1626).

Antipyrine, 1,2,3-Phenyldimethyl Pyrazolon, $\begin{array}{l} C_6H_5N—CO—CH \\ CH_3N=\!=\!=\!=CCH_3 \end{array}$, melting at 114°, is obtained in the form of its hydroiodide when phenylmethylpyrazolon is heated to 100°, together with methyl iodide and methyl alcohol. It also results by the condensation of symmetrical methylphenylhydrazine with acetoacetic ester (A. **238**, 160; B. **20**, R. 609):

$$\begin{array}{l} C_6H_5 . NH \\ CH_3 . NH \end{array} + \begin{array}{l} RO . CO . CH_2 \\ \qquad\;\; CO . CH_3 \end{array} = \begin{array}{l} C_6H_5N—CO—CH \\ CH_3N—\!—\!—CHCH_3 \end{array}.$$

Homologues of antipyrine are formed, similarly to it, from phenylmethylpyrazolon: **-2 Benzyl-** and **2-Ethyl-1-phenyl-3-methylpyrazolon**, *homoantipyrine*, melting at 119° and 73° respectively (J. pr. Ch. [2], **55**, 153; A. **293**, 3 Anm.).

Antipyrine is a strong monacid base. It is very soluble in water and alcohol, and crystallizes from ether in shining leaflets.

It is highly prized in medicine as an antipyretic. Its *salicylate*, **salipyrine**, acts similarly to it. This is also true of the homologue **tolypyrine** or γ-tolyldimethylpyrazolon, etc.

Antipyrine yields derivatives perfectly similar to those obtained from phenylmethylpyrazolon (B. **28**, 623). When antipyrine is boiled with alcoholic potash it is recon-

verted into phenylmethylhydrazine. On heating it with sodium in toluene, conducting carbon dioxide through it at the same time, the union between the two N-atoms is broken and β-methylamidocrotonic anilide is produced (B. **25**, 769):

$$\begin{array}{l} C_6H_5N{-}CO{-}CH \\ \vert \qquad\quad \Vert \\ CH_3N \text{———} C.CH_3 \end{array} \longrightarrow \begin{array}{l} C_6H_5.NH{-}CO{-}CH \\ \qquad\qquad\quad \Vert \\ CH_3NH \text{———} C.CH_3 \end{array}.$$

This is a rupture of a ring similar to that observed in the change of the pyrazolines to trimethylene diamines (p. 486).

4-**Nitrosoantipyrine**, $(C_{11}H_{11}N_2).NO$, results when antipyrine is acted upon with nitrous acid. Zinc and acetic acid reduce it to 4-**amido-antipyrine**, melting at 109°, the diazo-compounds of which are readily formed and yield dye-substances (A. **293**, 58).

4-**Oxyantipyrine**, melting at 182°, results from the methylation of 4-oxy-1-phenyl-3-methylpyrazolon (p. 488) and is a compound with a pronounced phenol character (A. **293**, 49).

At low temperatures methyl iodide converts antipyrine into *pseudo-iodmethylate*, having the formula, $\begin{array}{l} C_6H_5.N \text{———} C(OCH_3) = CH \\ \qquad\ \vert \qquad\qquad\quad \vert \\ INCH_3 = C(CH_3) \end{array}$, as it can also be prepared from methoxymethylphenylpyrazole and methyl iodide. At higher temperatures methyl iodide and antipyrine yield 4-**Methyl Antipyrine**, $\overline{CO.C(CH_3):C(CH_3).N(CH_3)N}.C_6H_5$, melting at 82°, and later 1-**Phenyl-3,4-trimethyl Pyrazolon**, $\overline{CO.C(CH_3)_2.C(CH_3):N.N}C_6H_5$, melting at 56° (A. **293**, 1). See C. 1897, I, 540, for the action of phenols upon antipyrine. Consult A. **293**, 42, for the addition of acid chlorides to antipyrine.

1-**Phenyl-5-methyl Pyrazolon**, $CH_3.\overline{C = CH - CO - NH.N}C_6H_5$, melting at 167°, is isomeric with 1-phenyl-3-methyl pyrazolon. It is produced when the corresponding pyrazolidone is oxidized with ferric chloride (B. **28**, R. 78). When it is methylated **isantipyrine** (B. **25**, R. 367; **28**, 629) results. This is isomeric with antipyrine, and it is *poisonous*.

Pyrazolon Carboxylic Acids: Their esters are obtained from the hydrazones of β-keto- or aldehydodicarboxylic esters. The acids readily break down into CO_2 and pyrazolons.

Pyrazolon-3-carboxylic Acid, $\overline{CO.CH_2 - C(COOH) = N - N}H$, decomposes at 250°. Its *methyl ester* melts at 227°. It is formed from oxalo-acetic methyl ester, chlorfumaric ester (B. **29**, R. 860), or acetylene dicarboxylic ester with hydrazine (B. **25**, 3442; **26**, 1722). Nitrous acid converts it into an *isonitroso*-compound, $\overline{CO - C(NOH).C(COOH) = N - N}H$, melting at 201°, which yields the hydrazide of *hydrazipyrazolon carboxylic acid* when treated with hydrazine hydrate. The *anhydride* of this acid, decomposing at 126°, represents a symmetrical dicyclic nucleus:

$$\begin{array}{l} N \text{======} C.COOH \\ \vert \qquad\qquad \vert \\ NH{-}CO{-}C = N.NH_2 \end{array} \xrightarrow{-H_2O} \begin{array}{l} N \text{======} C{-}CO{-}NH \\ \vert \qquad\qquad \vert \qquad\quad \vert \\ NH{-}CO{-}C \text{=====} N \end{array}$$

4-Hydrazi-pyrazolon-3-carboxylic Acid — Pyrazolonopyrazolon.

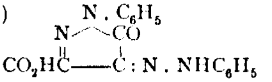
which may also be viewed as the dilactazam of dioxosuccinic osazone (B. **26**, 2057). By the elimination of carbon dioxide pyrazolon-3-carboxylic acid yields pyrazolon, obtained in various other ways (see B. **29**, 249).

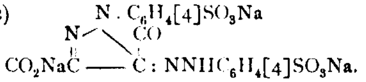
Pyrazolon-4-carboxylic Acid, $\overline{CO - CH(COOH) - CH = N.N}H$. Its *ethyl ester* melts at 181°. It is formed, along with malonyl hydrazides, when hydrazine hydrate acts upon the ester of dicarboxyglutaconic acid, $(CO_2R)_2CH.CH:C(CO_2R)_2$, and when

hydrazine and the ester of ethoxymethylenemalonic acid react (B. **28**, 1053). This acid splits off CO_2 quite easily and becomes pyrazolon (B. **28**, 988).

1-Phenylpyrazolon-4-carboxylic Acid, $\overline{CO - CH(COOH) - CH = N - NC_6H_5}$, melts at 93° with decomposition. Its *ethyl ester* melts at 118°. It is produced when phenylhydrazine acts upon the ester of dicarboxyl-glutaconic acid or the ester of ethoxymethylenemalonic ester (1, 494). The isomeric **1-Phenyl-3-pyrazolon Carboxylic Acid,** melting at 181°, is produced in the form of its ester from oxaloacetic ester and phenylhydrazine. Both phenylpyrazolon carboxylic acids yield the same phenylpyrazolon (p. 488; B. **28**, 41).

The ozazones of the dioxosuccinic acid esters readily yield the ester of **1-phenyl-4-phenylhydrazone-3-pyrazolon carboxylic acid** (1). This has a red color. It melts at 154°. It is the parent substance of the valuable yellow dye **tartrazine** (2), the chief constituent of which is the trisodium salt of **tartrazinic acid** or **1,p-sulphoxylphenyl-4,p-sulphoxylphenylhydrazono-pyrazolon-3-carboxylic acid**:

(1) 

(2) 

The latter acid can also be obtained from 1,p-sulphoxylphenyl-3-pyrazolon carboxylic acid and from the diazide of sulphanilic acid, which fully demonstrates its constitution (A. **294**, 219).

PYRAZOLIDINES.

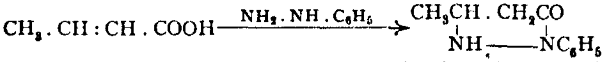
The derivatives of *tetrahydropyrazole* or *pyrazolidine* pass easily, as a general thing, into pyrazoline compounds, therefore they possess reducing properties. The simplest pyrazolidine is not yet known.

n-Phenylpyrazolidine, $\begin{matrix} NH - N . C_6H_5 \\ | \quad\quad | \\ CH_2 . CH_2 . CH_2 \end{matrix}$, is an oil. It boils at 160° (20 mm.). It is formed when sodium phenylhydrazine acts upon trimethylene bromide (B. **26**, R. 402). The oxygen of the air oxidizes it to phenylpyrazoline. Alkali and methyl iodide convert it into **1-Phenyl-2-methyl Pyrazolidine,** $\overline{CH_2 - CH_2 - CH_2 . N(CH_3)NC_6H_5}$, boiling at 175–180° (90 mm.). The reduction of the corresponding pyrazolidone produces **1-phenyl-3-methylpyrazolidine** (B. **26**, 107). **1,3,5-Triphenyl-2-methylpyrazolidine,** melting at 110°, results in the reduction of triphenylpyrazole iodmethylate with sodium and alcohol.

Pyrazolidine carboxylic acids have been obtained by the reduction of pyrazoline carboxylic acids (B. **26**, R. 282).

Keto-derivatives of the pyrazolidines:

(1) **Pyrazolidones** result from the interaction of hydrazines and β-haloid fatty acids or α,β-olefine carboxylic acids. If phenylhydrazine be employed, it is possible for the reaction to pursue a double course, according as the secondary or tertiary group of the hydrazine is rearranged by the carboxyl group of the acid:

(1) 

1-Phenyl-3-methyl-5-pyrazolidone

(2)

1-Phenyl-5-methyl-3-pyrazolidone.

The resulting isomerides are distinguished by the fact that the 1-phenyl-5-pyrazolidones have only *basic* properties, whereas the 1-phenyl-3-pyrazolidones also possess *acid* properties. On oxidation the pyrazolidones readily become pyrazolons, and when reduced with sodium and alcohol they are converted, in part, into pyrazolidines (see below).

Pyrazolidone, $CH_2 . CH_2 . CO . NH . NH$, boiling at 133–135°, is obtained from acrylic acid and hydrazine. It is a base. When oxidized it yields pyrazolon (J. pr. Ch. [2], 51, 73). **1-Phenyl-5-pyrazolidone**, $CO . CH_2 . CH_2 . NH . N . C_6H_5$, melting at 78°, is derived from β-haloid propionic acids by means of sodium formylphenylhydrazine, or from acrylic acid with phenylhydrazine in toluene solution (B. **28**, 26). It is only basic, and when oxidized it becomes 1-phenyl-5-pyrazolon, melting at 118° (p. 488).

The isomeric **1-Phenyl-3-pyrazolidone**, $CH_2 . CH_2 . CO . NH . N . C_6H_5$, melting at 119–121°, and obtained from β-haloid propionic acid with free phenylhydrazine, as well as from unsym. β-phenylhydrazidopropionic ester (B. **24**, R. 234), possesses acid properties also, and when oxidized becomes 1-phenyl-3-pyrazolon, melting at 154°; its n-*acetyl* derivative melts at 67° (B. **29**, 517).

1-Phenyl-3-methyl-5-pyrazolidone, melting at 84° and boiling at 321°, is derived from crotonic acid and phenylhydrazine or from symmetrical β-phenylhydrazidobutyric acid (B. **27**, R. 687). It is a base. It readily changes to 1,3-phenylmethylpyrazolon. When methylated it yields **1,2,3-phenyldimethylpyrazolidone**, *hydroantipyrine*, melting at 146°. It cannot be converted by oxidation into antipyrine (B. **26**, 103). **1-Phenyl-3-dimethyl-5-pyrazolidone**, $CO . CH_2 . C(CH_3)_2NH . NC_6H_5$, melting at 75°, is produced from dimethyl acrylic acid and phenylhydrazine. Boiling baryta-water decomposes it into phenylazoisovaleric acid, $C_6H_5N : N . C(CH_3)_2CH_2COOH$ (A. **292**, 284). **1-Phenyl-5-methyl-3-pyrazolidone**, melting at 128° and obtained from unsym. β-phenylhydrazidobutyric acid, also possesses acid properties. By oxidation it yields 1,5-phenylmethylpyrazolon (p. 488).

(2) *Diketopyrazolidines* are the cyclic hydrazides of the *malonic acids*: **3,5-Diketopyrazolidine**, *Malonyl hydrazine*, $CO . CH_2 . CO . NH . NH$, is an oil. It is formed from malonic ester and hydrazine (B. **28**, R. 159).

1-Phenyl-3,5-diketopyrazolidine, *Malonyl-phenylhydrazine*, melting at 192°, is obtained from the phenylhydrazide of malonic ester acid (B. **25**, 1506). Consult B. **30**, 1018, for its derivatives.

2. INDAZOLES.

Just as the benzopyrrols or indols correspond to the pyrrols, so do the benzopyrazoles or indazoles correspond to the pyrazoles.

There are two isomeric series of N-alkylic indazoles. The one series is produced by the action of alkyl iodides upon indazole or its homologues. The second series, called isindazoles, result synthetically from ortho-substituted α-alkylphenylhydrazines, and therefore have the alkyl residue attached to the N-atom adjacent to the benzene nucleus; consequently, in the isomeric n-alkyl indazoles the alkyl residue must be joined to the second (β-) N-atom, and the subjoined formula:

$C_6H_4 \langle \overset{CH}{\underset{N}{|}} \rangle NH$, must be ascribed to the simplest indazole from which the others are derived.

Hence the real benzopryazole, $C_6H_4 \langle {}^{CH}_{NH} \rangle N$, is the hypothetical parent-substance of the isindazoles.

Indazoles result (1) upon heating the o-hydrazine cinnamic acids (p. 277) (E. Fischer and Tafel, A. **227**, 303):

$$C_6H_4{<}{CH=CH.COOH \atop NH-NH_2} \longrightarrow C_6H_4{<}{CH \atop N}{>}NH\ (+\ CH_3.COOH)$$

o-Hydrazine-cinnamic Acid — Indazole.

It is singular that a lactam-like anhydride of the hydrazine-cinnamic acid is not formed in this reaction. It would contain a seven-membered ring (see p. 436). Indazole acetic acid is produced by the moderated oxidation of o-hydrazine-cinnamic acid.

(2) From the elimination of water from o-hydrazine-acetophenone or o-hydrazine-phenylglyoxylic acids:

$$C_6H_4{<}{CO.COOH \atop NH.NH_2} \longrightarrow C_6H_4{<}{C-COOH \atop N{>}NH}.$$

(3) n-Phenylindazoles are formed in the reduction of o-nitrobenzylanilines (B. **24**, 961; **27**, 2899):

$$C_6H_4{<}{CH_2-NHC_6H_5 \atop NO_2} \xrightarrow{H} C_6H_4{<}{CH \atop N}{>}NC_6H_5.$$

(4) Further, indazoles are formed by the careful decomposition of o-diazotoluene compounds (B. **26**, 2349):

$$(a)\ NO_2.C_6H_3{<}{CH_3 \atop N=NCl} \longrightarrow NO_2.C_6H_3{<}{CH \atop N}{>}NH$$

p-Nitro-o-diazotoluene Chloride — p-Nitroindazole.

$$(b)\ C_6H_4{<}{CH_3 \atop N=N.NHC_7H_7} \longrightarrow C_6H_4{<}{CH \atop N}{>}NH(+\ NH_2.C_7H_7)$$

Toluene-o-diazotoluide — Indazole.

Isindazoles are obtained (1) from o,a-alkylhydrazine-cinnamic acids or o,a-alkylhydrazine-acetophenones:

$$C_6H_4{<}{CH.CH.COOH \atop NR.NH_2} \rightarrow C_6H_4{<}{CH{\searrow}N \atop N{\swarrow}R};\quad C_6H_4{<}{CO.CH_3 \atop NR.NH_2} \rightarrow C_6H_4{<}{C(CH_3){\searrow} \atop NR{-\!\!-}{\nearrow}}N.$$

(2) By the action of glacial acetic acid or acetic anhydride upon o-amidoaldoximes or ketoximes (B. **26**, 1903; **29**, 1261):

$$C_6H_4{<}{C:NOH \atop NH_2} \xrightarrow{(CH_3CO)_2O} C_6H_4{<}{CH= \atop N(COCH_3)}{>}N.$$

(3) The formation of an imidazole derivative from the phenylhydrazone of o,p-dinitrophenylglyoxylic ester recalls pyrazole syntheses (B. **22**, 319):

$$NO_2.C_6H_3{<}{C(CO_2R):N.NHC_6H_5 \atop NO_2} + KOH = NO_2.C_6H_3{<}{C(CO_2R) \atop N(C_6H_5)}{>}N + NO_2K + H_2O.$$

a-Phenylisindazole, $C_6H_4{<}{CH= \atop N(C_6H_5)}{>}N$, *melting at* 142° (C. 1897, 1, 763), is similarly formed from salicylaldehyde and phenylhydrazine by the action of acetic anhydride.

Properties. The indazoles are usually crystalline, feeble bases, quite stable toward oxidizing agents. Chromic acid decomposes β-phenylindazole into azobenzene-carboxylic acid. Hydro-compounds are obtained with difficulty. The free imide-group can be alkylized by alkyl iodides at 100°. The isindazoles resemble the indazoles in general characteristics. The substituents of the pyrazole ring, proceeding from the nitrogen attached to the benzene nucleus, are designated with Iz- a-, β-, γ-; and those of the benzene ring, Bz- 1, 2-, 3-, 4-.

Indazole, $C_7H_6N_2$, melting at 146° and boiling at 270°, is produced, in addition to the reactions already given, by diazotizing o-amidobenzaldehyde (B. **25**, 1754). Sodium nitrite converts it into *nitrosoindazole*, $C_7H_5N_2.NO$, melting at 74°. **γ-Methyl Indazole**, $C_7H_6(CH_3)N_2$, melting at 113° and boiling at 281°, is obtained from o-hydrazine-acetophenone. Acetyl chloride converts it into *β-acetyl-γ-methyl indazole*, $C_7H_4(CH_3)N_2.COCH_3$, melting at 72° (B. **24**, 2380). It forms—

β,γ-Dimethyl indazole, $C_7H_5(CH_3)N_2 . CH_3$, melting at 80°. **β-Phenyl-indazole** $C_7H_5N_2 . C_6H_5$, melting at 84° and boiling at 345°, is formed from nitrobenzyl aniline (comp. p. 492). Methyl iodide unites with it to an *iodmethylate*, melting at 188°, and is oxidized by chromic acid to azobenzene-carboxylic acid (B. **24**, 3058; **27**, 48). **γ-Phenyl-indazole,** melting at 108° or 116°, is produced by the reduction of o-diazobenzophenone. When sodium sulphite is used for this purpose there first results an oxygen-containing body, $C_{13}H_{10}N_2O$, melting at 126°, which probably is a **β-oxy-γ-phenyl-indazole,** that upon further reduction becomes phenyl indazole (B. **29**, 1265). **Bz-2-Nitro-indazole,** $NO_2 . C_6H_3(CN_2H_2)$, melting at 181°, is formed, together with nitrocresol (B. **26**, 2349), upon diazotizing nitro-o-toluidine. Bz-**1,3-Nitromethyl Indazole,** melting at 192°, is obtained from nitroxylidine (B. **29**, 305).

γ-Indazole Carboxylic Acid, $C_7H_5N_2 . COOH$, melting with decomposition at 259°, is derived from o-hydrazine-phenyl-glyoxylic acid, which is prepared from isatinic acid (p. 258), thus completing the transition from the indol to the indazole group (B. **26**, 217). When the acid is heated it breaks down into indazole and carbon dioxide.

γ-Indazole Acetic Acid, $C_7H_5N_2 . CH_2 . COOH$, results from the moderated oxidation of o-hydrocinnamic acid. It melts at 169°, and decomposes into carbon dioxide and γ-methyl indazole.

α,γ-**Dimethyl Isindazole,** $C_6H_4\begin{matrix}\diagup C(CH_3) \diagdown \\ \diagdown N(CH_3) \diagup\end{matrix}N$, melting at 36°, is made by the reduction of nitroso-o-ethylamido-acetophenone. Iz-α-**Acetyl Isindazole,** $C_7H_5N_2 . COCH_3$, Iz-α-γ-**Acetyl Methyl-** and α,γ-**Acetyl Phenyl Isindazole,** melting at 103° and 185°, are formed by method 2 (p. 492) from o-amido-benzaldoxime, -acetophenonoxime, and -benzophenonoxime. Alkalies again resolve them into these oximes (B. **29**, 1255). α-**Ethyl-γ-isindazole Acetic Acid,** $C_7H_4N_2(C_2H_5)(CH_2 . COOH)$, melting at 132°, is obtained from nitroso-o-ethylamido-cinnamic acid. See above for α-**phenyl isindazole** and **nitro-α,γ-phenyl isindazole carboxylic acid.**

Hydro-isindazole Derivatives: β **Phenyl Dihydroïndazole,** $C_6H_4\langle\begin{matrix}CH_2\\NH\end{matrix}\rangle N . C_6H_5$, melting at 138°, is produced by the reduction of phenyl indazole with sodium and alcohol.

Bz-Nitro-α-phenyl Dihydroindazole-γ-carboxylic Acid, melting at 235°, is formed in the reduction of nitrophenyl indazole carboxylic acid (A. **264**, 149).

Indazolon, or *Benzo-pyrazolon*, is the inner anhydride or lactazam of o-hydrazine-benzoic acid, $C_6H_4<\begin{matrix}CO\\NH\end{matrix}>NH$ (A. **213**, 333).

Nitro-Iz,β-phenyl Indazolon is formed from the ester of nitrophenyl hydrazidobenzoic acid (B. **30**, 1100). We must include here **Camphylphenylpyrazolon Carboxylic Ester,** $C_8H_{14}\begin{matrix}\diagup C\text{———}C\text{———}CO_2R \\ \| \\ \diagdown C{-}N(C_6H_5){-}N\end{matrix}$, melting at 114°, which is formed from the ester of camphor-oxalic acid and phenylhydrazine (C. 1897, II, 123).

The following are *benzodipyrazolons:*

Hexahydrobenzodipyrazolon, $NH\begin{matrix}\diagup CO \diagdown \\ \diagdown N \diagup\end{matrix}C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown N \diagup\end{matrix}NH$, melting at 275°, is obtained from the ester of succino-succinic acid and hydrazine.

Dicarbobenzobis-n-phenylpyrazolon, $(COOH)_2C_6\left(\begin{matrix}-CO\\-NH\end{matrix}>NC_6H_5\right)_2$, is produced by the interaction of phenylhydrazine and hydroquinone tetracarboxylic ester (Am. Ch. J. **12**, 379).

3. ISOXAZOLE OR FURO[a]MONAZOLE GROUP.

Isoxazole is the azole of furfurane corresponding to pyrazole or pyrro-[α]-monazole: *Furo*-[a]-*monazole*. In accordance with similar structure the isoxazoles are produced by methods similar to those employed for the

preparation of the pyrazoles. The latter, as known, are obtained from the hydrazones of β-diketo-compounds, and accordingly the isoxazoles result by the exit of water from the monoximes of β-diketones and β-ketone aldehydes or oxymethylene ketones (Claisen, B. **24**, 3906):

$$\underset{\text{Benzoylacetophenone Monoxime}}{\begin{matrix} C_6H_5C-CH_2-CO.C_6H_5 \\ \| \\ N.OH \end{matrix}} \longrightarrow \underset{\alpha,\gamma\text{-Diphenyl Isoxazole.}}{\begin{matrix} C_6H_5C-CH=C.C_6H_5 \\ \| \qquad\qquad | \\ N\text{———}O \end{matrix}}$$

Compare B. **24**, R. 767, for the formation of isoxazoles from nitroparaffins by the action of alkalies.

Properties: Those isoxazoles, in which the adjacent methine group of the N-member is substituted, are very stable bodies. When this CH-group is not substituted, a *rearrangement* of β-ketonic acids into nitriles occurs quite readily, especially under the influence of sodium alcoholate:

$$\underset{\alpha\text{-Phenylisoazole}}{\overline{N=CH-CH=C(C_6H_5)O}} \longrightarrow \underset{\text{Benzoyl Acetonitrile.}}{N\equiv C-CH_2-C(C_6H_5)=O}$$

The isoxazoles, like the pyrazoles, are feeble bases. The substituents of the simplest hypothetical isoxazole are designated in the diagram:

$$\begin{matrix} \gamma CH=N \\ | \\ \beta CH=CH_\alpha \end{matrix} \!\!>\! O.$$

γ-**Methyl Isoxazole,** $\overline{N=C(CH_3)-CH=CH-O}$, boiling at 118°, is stable. It results when hydroxylamine acts upon oxymethylene acetone. There is formed at the same time the isomeric α-**Methyl Isoxazole,** $\overline{N=CH-CH=C(CH_3)-O}$, boiling at 123°, which readily rearranges itself to the nitrile of acetic acid (B. **25**, 1787).

α-β,γ-**Trimethyl Isoxazole,** $\overline{N=C(CH_3)-C(CH_3)=C(CH_3)-O}$, melting at 3.5° and boiling at 248°, results from the action of alkalies upon methylacetylacetoxime and from nitroethane (J. Ch. Soc. **1891**, 410).

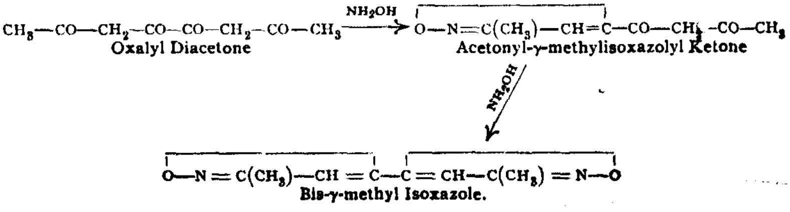
See B. **24**, 3912, for ring decompositions in consequence of reductions. **Phenyl Methyl Isoxazole,** melting at 68°, is obtained from benzoyl acetone (p. 250). When heated with alcoholic ammonia it yields 3,5-phenylmethyl pyrazole (p. 482).

Isoxazole Carboxylic Acids.—Their esters are prepared from the oximes of the ketone-oxalic esters:

$$\underset{\text{Acetone Oxalester Oxime}}{(CH_3)CO-CH_2-C(COOR)=N.OH} \longrightarrow \underset{\beta,\gamma\text{-Isoxazole Carboxylic Ester.}}{\overline{(CH_3)C=CH-C(COOR)=N-O}}$$

The free acids cannot be decomposed into carbon dioxide and isoxazoles. They are completely broken down when heated (B. **24**, 3908).

Bis-isoxazoles result from the interaction of oxalyldiketones and hydroxylamine:



Acetonyl-γ-methylisoxazolyl Ketone appears as an intermediate product. It can also be made by the condensation of γ-methylisoxazole-α-carboxylic ester with acetone (B. **24**, 3910).

Isoxazolons.—These are keto-derivatives of the hypothetical dihydro-isoxazole or isoxazoline. They correspond to the pyrazolons or lactazams, consequently can also be designated as *lactazones* or *lactoximes*. They result when the oximes of the β-ketonic esters lose alcohol (B. **24**, 140; **30**, 1159; A. **296**, 33):

$$HO.N=C(CH_3).CH_2—COOR \longrightarrow \overline{O.N=C(CH_3)—CH_2—CO}.$$

A series of compounds, obtained from glyoxal, methylglyoxal, phenylglyoxal, etc. (also their oximes), by the action of hydroxylamine hydrochloride, can also be considered as the oximes of isoxazolon derivatives (comp. B. **30**, 1287).

The isoxazolons, similarly to the pyrazolons, can be variously formulated:

$$\text{I. } \begin{matrix} CH_2—CO \\ | \\ CH=N \end{matrix} \!\!>\! O \qquad \text{II. } \begin{matrix} CH—CO \\ \| \\ CH—NH \end{matrix} \!\!>\! O \qquad \text{III. } \begin{matrix} CH=C(OH) \\ | \\ CH=\!=\!=N \end{matrix} \!\!>\! O.$$

The isoxazolons have a very pronounced acid nature. They decompose the alkaline earth carbonates in the cold, and form salts not only with metals, but also with ammonia and primary amines. The constitution of these salts varies. Ethers result from the action of alkyl iodides upon the silver salts. Methylamine is liberated when phenyl-isoxazolon-methyl ether is distilled with caustic potash. The methyl group is therefore probably linked to nitrogen, and the compound is derived from formula II (A. **296**, 37).

γ-**Methyl Isoxazolon**, $C_4H_5NO_2$, melting at 170°, is made from the oxime of aceto-acetic ester. *Barium salt*, $(C_8H_7O_3N_2)_2Ba + 1\frac{1}{2}H_2O$. The *ammonium salt*, $(C_8H_7O_3H_2)NH_4$; *methyl ester*, $(C_8H_7O_3N_2)CH_3$ (A. **296**, 46). When the oxime of aceto-acetic ester is condensed in the presence of diazobenzene salts the *phenylhydrazone* of *γ-methyl-*p*-ketoisoxazoline*, $(C_4H_3NO_2):NNHC_6H_5$, melting at 192°, results. The condensation of the same oxime in the presence of ketones or aldehydes gives rise to **Isopropylidene** and **Benzylidene Methyl Isoxazolons**, $(C_4H_3NO_2):C(CH_3)_2$, melting at 121°, and $(C_4H_3NO_2):CH.C_6H_5$, melting at 141° (B. **30**, 1337).

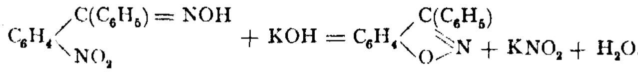
Isonitrosomethyl-isoxazolon—compare B. **28**, 2093; **30**, 1342. γ-**Phenyl Isoxazolon**, $C_9H_7NO_2$, melts at 152°. *Silver salt*, $C_9H_6NO_2Ag$; *aniline salt*, $C_9H_7NO_2.NH_2C_6H_5$, melts at 111°. *Methyl ester*, $C_9H_6NO_2.CH_3$, melts at 78°. The action of benzoyl chloride and alkali produces two *benzoyl esters* of phenyl isoxazolons, insoluble in alkalies, melting at 161° and 115° (B. **30**, 1614). β,γ-**Dimethyl Isoxazolon** melts at 124°. γ,β-**Methyl Ethyl Isoxazolon** melts at 50° (A. **296**, 56). γ,β-**Methyl Benzyl Isoxazolon** melts at 106° (B. **30**, 1161). γ-**Phenyl-α-imido-isoxazolin**, $\overline{O—N=C(C_6H_5)—CH—C}:(NH)$, melting at 111°, results from cyanacetophenone, $C_6H_5.CO.CH_2.CN$, or benzodiacetonitrile and hydroxylamine (B. **27**, 1095; Jr. pr. Ch. [2], **47**, 124). γ-**Phenyl-α-benzoyl-β-isoxazolon**, melting at 175°, is obtained from benzoyl formoïn (p. 381) and hydroxylamine (B. **25**, 3468; compare B. **30**, 1290):

$$\underset{\text{Benzoyl Formoïn}}{C_6H_5CO—CO—CH(OH)—CO.C_6H_5} + NH_2OH \longrightarrow \underset{\text{Phenylbenzoyl-β-isoxazolon.}}{\overline{O—N=C(C_6H_5)—CO—CH}.CO.C_6H_5}$$

Compare B. **30**, 1085, for the so-called **pyroxolon carboxylic ester**, $C_3H_2NO_2.CO_2R$, a reaction product of hydroxylamine and the ester of dicarboxyglutaconic acid.

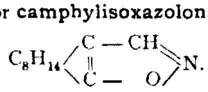
4. INDOXAZENE OR BENZISOXAZOLE GROUP.

The benzisoxazoles or indoxazenes are obtained from the oximes of o-haloid or o-nitrobenzophenones (p. 347; B. **25**, 1498) (compare method of formation 3 under the isindazoles, p. 492):



The simplest indoxazene, which should arise from brom- or o-nitrobenzaldoxime, appears not to be stable, as it immediately rearranges itself into salicylnitrile (compare isoxazoles, p. 494) (B. **26**, 1253). **Phenyl Indoxazene,** $C_{13}H_9NO_2$, melting at 84° and boiling at 331-336°, yields a dinitro-derivative with fuming nitric acid. When it is reduced with sodium and alcohol it decomposes into o-phenobenzylamine, $C_6H_4<^{CH(C_6H_5)NH_2}_{OH}$, while HI and phosphorus change it to o-benzoylphenol (B. **28**, R. 604; **29**, R. 350). Consult B. **27**, 1452; **28**, 1872, R. 290, for other indoxazene derivatives.

Compare C. 1897, II, 123, for **camphylisoxazolon,**

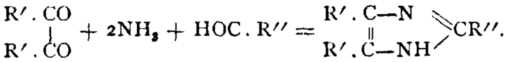


5. GLYOXALINES OR IMIDAZOLES.

Glyoxaline or imidazole is metameric with pyrazole; like the latter, it may be viewed as a ring-azo-substitution product of pyrrol, and hence be designated as *pyrro-*[b]*-monazole*, $\overset{CH = CH}{\underset{N \!=\!=\! CH}{|}} \!>\! NH$. Again, the glyoxalines may be considered cyclic amidines, just as is done with ring-homologous pyrimidines.

History: Debus (1856) discovered glyoxaline as a reaction product of ammonia and glyoxal. Radziszewski (1882) explained this reaction and applied it to other diketones. Those peculiar bases—the *oxalines*—prepared by Wallach (1876) from the dialkyloximide chlorides were found later to be glyoxalines. Japp (1882), cognizant of the relations existing between the lophines and glyoxalines, made them the basis for the constitution formula of the glyoxalines accepted to-day almost universally. Indeed, it has been established by the more recent syntheses of Wohl and Markwaldt, and of Bamberger.

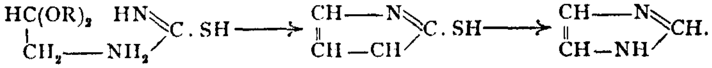
Glyoxalines result (1) from the condensation of glyoxal and other o-diketo-compounds with ammonia and aldehydes (B. **15**, 2706):



Glyoxaline is formed when ammonia acts upon glyoxaline. This is dependent upon a partial decomposition of the glyoxal into formic aldehyde and formic acid.

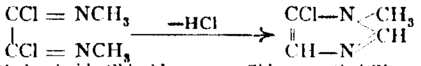
Allied to this reaction is the production of glyoxalines from 1,2-diketones and amines of the formula $RCH_2 . NH_2$. Benzil and benzylamine yield *triphenyl* n-*benzyl-glyoxaline*, while with ethylamine the product is *diphenyl-μ-methyl-*n*-ethyl glyoxaline* (B. **28**, R. 302).

(2) Acetyl- and acetonyl thioureas and similar bodies yield, by inner condensation, mercaptans of glyoxalines, which, upon oxidation, part with H_2SO_4 and become glyoxalines (B. **22**, 1353; **25**, 2354; **26**, 2204):



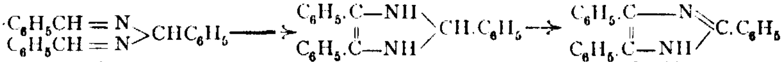
Triphenyl glyoxaline is similarly produced from benzoïn and benzamidine (B. **29**, R. 673).

(3) The alkylimide chlorides of oxalic acid, by peculiar reactions, change to chlor-substitution products of the glyoxalines and yield the latter upon reduction (A. **214**, 278):



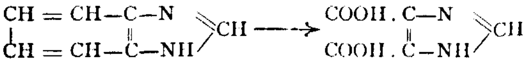
Dimethyl-oximide Chloride α-Chlor-n-methyl Glyoxaline.

(4) Hydrobenzamide (p. 184) and similarly constituted aromatic amines, when heated, rearrange themselves to dihydroglyoxalines, which readily change to glyoxalines:



Hydrobenzamide Amarine, Triphenyldihydro-glyoxaline Lophine, Triphenyl-glyoxaline.

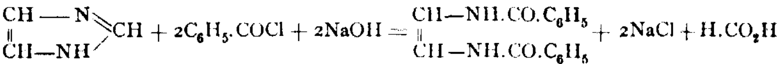
(5) A very interesting formation, theoretically speaking, of glyoxaline carboxylic acid consists in oxidizing benzoglyoxaline or benzimidazole with potassium permanganate (A. **273**, 339):



Benzimidazole Imidazole Dicarboxylic Acid.

(6) Certain imidazoles have been obtained from the corresponding oxazoles on heating them with ammonia (B. **29**, 2098).

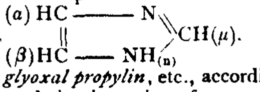
Properties.—The glyoxalines are stronger bases than the isomeric pyrazoles. Their imide hydrogen can be replaced by metals, especially silver, and also by alkyl residues through the agency of alkyl iodides. The tertiary bases take up alkyl iodides very energetically. The n-alkyl glyoxalines are rearranged on heating, the alkyl residue migrating to the (μ) C-atom, occupying the position between the two N members. Acidyl-groups are only introduced with difficulty and are easily split off. Benzoyl chloride and sodium hydroxide occasion, rather strangely, even at 0°, decomposition into carboxylic acids and dibenzoyldiamines:



Glyoxaline Dibenzoyldiamidoethylene.

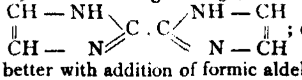
The glyoxalines are very stable toward reducing agents, and are but slightly altered by oxidants. Hydrogen peroxide produces oxamides.

The position of the substituents in glyoxaline is indicated in the following manner:



The μ-alkyl derivatives are also termed *glyoxal ethylin*, *glyoxal propylin*, etc., according to the aldehyde used in the synthesis, as they are chiefly made by the action of ammonia and aldehydes upon glyoxal.

Glyoxaline, Imidazole, $C_3H_4N_2$, melting at 90° and boiling at 263°, is formed, together with *glycosine* (probably **bisglyoxaline,**



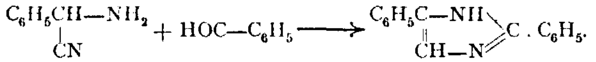
; compare B. **20**, R. 431), from glyoxal and ammonia, better with addition of formic aldehyde (A. **277**, 336); also from imidazolyl-μ-mercaptan, as well as from its carboxylic acid. It is soluble in alcohol, ether, and water. Its solutions containing alkali phosphoresce on exposure to the air (compare lophine). It forms salts with all acids excepting carbonic acid. Silver nitrate precipitates *silver glyoxaline*, $C_3H_3N_2Ag$, and methyl iodide forms **n-Methyl Glyoxaline,** $C_3H_3N_2CH_3$, melting at —6° and boiling at 199°, with sp gr. 1.0363. This can also be obtained from dimethyloximide chloride according to method of formation 3 (above). **n-Phenyl Glyoxaline,** $C_3H_3N_2 . C_6H_5$, melting at 13° and boiling at 276°, is formed by method 2 (p. 496) from its mercaptan.

μ-**Methyl Glyoxaline,** *Glyoxal Ethylin, Paraglyoxal Methylin,* $C_3H_3(CH_3)N_2$, melting at 137° and boiling at 267°, results from the rearrangement of n-methyl glyoxaline (see above), or from glyoxal, acetaldehyde, and ammonia. Ethyl iodide converts it into *μ*-**Methyl-n-ethyl Glyoxaline,** $C_3H_2(CH_3)N_2 . C_2H_5$, boiling at 213°, which is also formed from diethyl oximide chloride, and manifests physiological actions similar to those of *atropine*. *μ*-**Ethyl Glyoxaline,** *Glyoxal Propylin,* $C_3H_3(C_2H_5)N_2$, melts at 80° and boils at 268°.

α-**Methyl Glyoxaline,** $C_3H_3(CH_3)N_2$, boils at 263°. It is prepared from its mercaptan by method 2 (p. 496) (B. **26**, 2204).

α,β,μ-**Trimethyl Glyoxaline,** $C_3(CH_3)_3N_2H$, melting at 183° and boiling at 271°, is made from diacetyl, ammonia, and aldehyde.

β,μ-**Diphenyl Glyoxaline,** $C_3H(C_6H_5)_2N_2H$, melting at 162°, is produced on heating *β,μ*-diphenyl oxazole (p. 503) to 300° with alcoholic ammonia; also by the condensation of phenyl-*α*-amidoacetonitrile and benzaldehyde by means of hydrochloric acid (compare method of forming oxazoles, p. 502) (B. **29**, 2103):



α,β,μ-**Triphenyl Glyoxaline, Lophine,** melting at 275°, is produced:

(1) From benzil, benzaldehyde, and ammonia.

(2) When hydrobenzamide is distilled or amarine oxidized.

(3) By the reduction of triphenyl cyanidine or triphenyl tricyanogen; ammonia is eliminated.

(4) From benzamidine and benzoïn (B. **29**, R. 673).

Lophine (from λόφος, tuft of feathers, alluding to its tufted crystalline form) exhibits in marked degree the property of phosphorescing when shaken with alcoholic potash; it is then decomposed into ammonia and benzoic acid. Like the glyoxalines, it does not form an acetate.

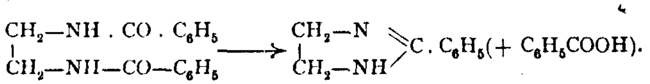
The halogen derivatives of the glyoxalines result from substitution; also by the splitting-off of hydrogen chloride from the dialkyloximide chlorides. **Tribrom-glyoxaline,** $C_3Br_3N_2H$, melting at 214°, is formed from glyoxaline and bromine. **Chlor-n-methyl Glyoxaline,** $C_3H_2ClN_2 . CH_3$, boiling at 205°, and **Chlor-n,*μ*-dimethyl Glyoxaline,** $C_3HCl(CH_3)N_2 . CH_3$, boiling at 218°, are obtained from dimethyl- and diethyloximide chloride.

Sulphydro-derivatives are formed by condensation from acetalyl or acetonyl thioureas and similar bodies (p. 496):

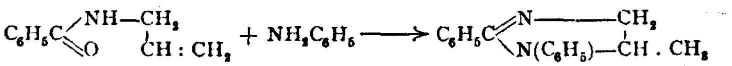
μ-**Imidazolyl Mercaptan,** $C_3H_3(SH)N_2$, melting at 222° with decomposition, is changed by methyl iodide to **imidazolyl-*μ*-methyl sulphide,** $C_3H_3(SCH_3)N_2$, melting at 139° (B. **25**, 2359). *α,β*-**Diphenyl Glyoxaline-*μ*-mercaptan,** $C_3(C_6H_5)_2HN_2(SH)$, is formed by the interaction of benzoïn and thiourea (A. **284**, 8).

α,β-**Glyoxaline Dicarboxylic Acid,** $C_3H_2(COOH)_2N_2$, is obtained from dioxytartaric acid, ammonia, and formaldehyde (A. ch. ph. **24**, 525), and by oxidizing benzoglyoxaline (A. **273**, 339). It breaks down, on heating, into CO_2 and glyoxaline.

Hydroglyoxalines.—The glyoxalines cannot be reduced to hydro-derivatives. *Dihydroglyoxalines,* or *glyoxalidines,* result (1) from the acidyl-compounds of ethylene diamine:



(2) They are very probably the compounds formed from allyl acetamide and allyl benzamide by means of the hydrochlorides of aromatic bases (B. **28**, 1665):



Allyl Benzamide **α-Methyl-μ,n-diphenyl Glyoxalidine.**

μ-Methyl Glyoxalidine, *Lysidine*, $C_4H_8N_2 = \begin{matrix} CH_2-N \\ | \\ CH_2-NH \end{matrix} \!\!>\! C.CH_3$, melting at 105° and boiling at 195–198°, is formed on heating ethylenediamine hydrochloride with sodium acetate. It forms a *very easily soluble uric acid salt*, and therefore has been recommended as a relief from gout (B. 27, 2952). The homologous glyoxalidines—*e.g.*, **μ-ethyl-, μ-propyl glyoxalidine**, etc., (B. 28, 1173, 1176)—behave similarly. Benzoyl chloride and alkali resolve methyl glyoxalidine into acetdibenzoyl ethylene diamine (B. 28, 3068).

μ-Phenyl Glyoxalidine, *Ethylenebenzamidine*, $C_3H_5(C_6H_5)N_2$, melting at 101°, is also obtained from ethylenediamine and thiobenzamide (B. 25, 2135).

α,β,μ-Triphenyl Dihydroglyoxaline, Amarine,

$C_{21}H_{18}N_2 = \begin{matrix} C_6H_5.C-NH \\ \| \\ C_6H_5.C-NH \end{matrix} \!\!>\! CH.C_6H_5$, melting at 113°, results from the rearrangement of hydrobenzamide. Alkyl iodides convert it into dialkyl derivatives, hence it must contain two imide groups. It yields lophine upon oxidation (p. 498). *Furfurin*, or *trifuryldihydroglyoxaline*, is analogously constituted (p. 450).

Bisglyoxalidine, $(C_3H_5N_2)_2$, melting at 290–300°, is a condensation product of rubeanic acid and ethylenediamine (B. 24, 1846):

$$\underset{\text{Rubeanic Acid}}{NH_2.CS-CS.NH_2} + 2NH_2.CH_2.CH_2.NH_2 \longrightarrow \underset{\text{Bisglyoxalidine.}}{NH-CH_2-CH_2-N=C-C=N-CH_2-CH_2-NH}$$

Tetrahydroglyoxalidines have been obtained from ethylene aniline and aldehydes (B. 20, 732):

$$\begin{matrix} CH_2-NH.C_6H_5 \\ | \\ CH_2-NH.C_6H_5 \end{matrix} + CHO.C_6H_5 = \begin{matrix} CH_2-N(C_6H_5) \\ | \\ CH_2-N(C_6H_5) \end{matrix} \!\!>\! CH(C_6H_5)$$

Triphenyltetrahydroglyoxaline, m. p. 137°.

We must include with the *keto-*, *thio-*, and *imido*-substitution products of hydroglyoxalines a series of cyclic urea-, thiourea-, and guanidine-derivatives, which for the most part have been already described with the fatty compounds.

1. *Ketoglyoxalidines*, *imidazolons*, or *ureïnes*, result from the inner condensation of α-ureïdo-keto-compounds: **Imidazolon**, $\begin{matrix} CH-NH \\ \| \\ CH-NH \end{matrix} \!\!>\! CO$, melting at 105°, is obtained from acetyl urea (p. 496). Different ureïnes have been obtained from benzoïn and benzil by means of various ureas (compare B. 25, 2357; 27, 1083, 1144, 2203; Gaz. chim. Ital. 19, 573).

2. *Keto-* and *Thiotetrahydroglyoxalines* are the cyclic alkylen ureas and thioureas—*e.g.*, *ethylene urea* and *-thiourea* (1, 400, 409).

3. *Diketo-* and *imidoketotetrahydroglyoxalines* are found in the hydantoïns and *glycocyanidines*—*e.g.*, *hydantoïn*, *creatinine*, etc. (1, 401, 413).

4. *Triketo-* and *imidodiketotetrahydroglyoxalines*: *oxalyl urea* or *parabanic acid* (1, 505) and *oxalyl guanidine* (B. 26, 2552).

6. BENZOGLYOXALINES, OR BENZIMIDAZOLES.

The benzimidazoles, sometimes called cyclic amidines, anhydro-bases, and aldehydines, contain the glyoxaline or imidazole ring in union with a benzene ring:

$$\begin{matrix} CH=CH-C-N \\ | \qquad\quad \| \\ CH=CH-C-NH \end{matrix} \!\!>\! CH.$$

Their intimate connection with glyoxaline becomes very evident from the fact that benzimidazole becomes glyoxaline dicarboxylic acid when it is oxidized (p. 496).

Formation of the Benzimidazoles :

(1) By the condensation of o-phenylenediamines with carboxylic acids, or their anhydrides or chlorides. An exit of water occurs (Ladenburg, B. **8**, 677; **11**, 826). Acidyl compounds are produced at the same time as intermediate products:

$$\underset{\text{o-Phenylenediamine}}{C_6H_4<^{NH_2}_{NH_2}} + CH_3.COOH \longrightarrow \underset{\text{Acetyl-o-phenylenediamine}}{C_6H_4<^{NH.CO.CH_3}_{NH_2}} \longrightarrow \underset{\mu\text{-Methylbenzimidazole.}}{C_6H_4<^{NH}_{N}\!\!>C.CH_3}$$

The diacidyl-o-phenylenediamines also yield benzimidazoles (B. **23**, 1876; **25**, 1992). The anhydrides of dibasic acids react like those of the monobasic—*e. g.*, succinic anhydride and o-phenylenediamine form benzimidazole-μ-propionic acid (B. **27**, 2773). The o-naphthylenediamines behave like the o-phenylenediamines.

(2) Benzimidazoles are also produced by the reduction of acidylated o-nitranilines, when acidylated o-phenylenediamines are also formed as intermediate products (Hobrecker, B. **5**, 920):

$$C_6H_4<^{NH.CO.CH_3}_{NO_2} \longrightarrow \left[C_6H_4<^{NH.CO.CH_3}_{NH_2}\right] \longrightarrow C_6H_4<^{NH}_{N}\!\!>C.CH_3.$$

(3) N-alkylic benzimidazoles result when *aldehydes* act upon o-diamines (*aldehydines* of Ladenburg, B. **11**, 590). The dialkylidene-o-diamine, which probably first appears, rearranges itself at once into the n-alkylic imidazole (B. **20**, 1585). The non-alkylized imidazole is produced as a by-product from the monoalkylidene body:

$$C_6H_4<^{N=CH.CH_3}_{N=CH.CH_3} \longrightarrow C_6H_4<^{N}_{N-CH_2.CH_3}\!\!>C.CH_3$$

$$C_6H_4<^{N=CH.CH_3}_{NH_2} \xrightarrow{-2H} C_6H_4<^{N}_{NH}\!\!>C.CH_3.$$

Mono-alkylic o-diamines yield benzimidazoles (B. **25**, 2826).

Properties: The benzimidazoles behave very much like the glyoxalines (p. 496); however, the basic properties are slightly less than the salt-forming power of the imido-group. Most of the benzimidazoles are soluble in aqueous alkalies. Alkyl residues are easily introduced into the imide group; acid residues, with more difficulty. Benzoyl chloride and sodium hydroxide decompose even at 0°, just as in the case of the glyoxalines, the imidazole ring with the production of dibenzoylated o-diamines. They are very stable toward reducing and oxidizing agents. Certain derivatives of benzimidazole can dye cotton without the help of mordants (B. **26**, 2760). In this respect they resemble the benzoxazoles (p. 503) and benzothiazoles (p. 507).

The number of known benzimidazoles is very great. See Kühling: Stickstoffhaltige Ortho-condensationsproducte, S. 177–210.

Benzimidazole, o-*Phenylene Formamidine*, $C_6H_4<^{N}_{NH}\!\!>CH$, melting at 167°, is obtained from formic acid and o-phenylenediamine, as well as by the action of chloroform and potash upon o-phenylenediamine (B. **28**, R. 392). Potassium permanganate oxidizes it in part to glyoxaline dicarboxylic acid. **μ-Methyl-benzimidazole**, o-*phenylene acetamidine*, $C_6H_4<^{N}_{NH}\!\!>C.CH_3$, melts at 176°.

μ-Phenylbenzimidazole, *phenylene benzamidine*, $C_6H_4<^{N}_{NH}\!\!>C.C_6H_5$, melting at 291°, also results from the rearrangement of o-amidobenzophenonoxime (B. **24**, 2386; **29**, R. 358).

μ-**Methyl Tolimidazole**, o-*Toluylene Acetamidine*, $CH_3 . C_6H_3 . \langle{}^{N=}_{NH}\rangle C . CH_3$, melting at 199°, and obtained from m,p-toluylenediamine with glacial acetic acid or acetaldehyde, unites with methyl iodide to n,*μ*-**dimethyl tolimidazole**, melting at 142°, then to its *iodmethylate*, melting at 221°. Silver nitrate precipitates the *silver salt*, $C_7H_6(C_2H_3N_2Ag)$. Chloride of lime replaces the imide hydrogen by chlorine, which readily exchanges its place with a benzene hydrogen atom:

$$C_7H_6 < {}^{N=}_{NCl} > C . CH_3 \longrightarrow C_7H_5Cl < {}^{N=}_{NH} > C . CH_3.$$

This chlorination may be continued until all of the hydrogen atoms of the benzene nucleus have been replaced by chlorine and there is finally obtained

n-**Chlor-*μ*-methyl Trichlorimidazole**, $CH_3 . C_6Cl_3 \langle{}^{N=}_{NCl}\rangle C . CH_3$.

n-*Acetyl-μ-methyl Tolimidazole*, $C_7H_6(C_2H_3N_2 . COCH_3)$, is formed when acetyl chloride acts upon the silver salt. The n-*benzoyl derivative*, melting at 92°, is formed from the base and benzoyl chloride, while benzoyl chloride and sodium hydroxide produce dibenzoyltoluylenediamine. *μ*-Methyltolimidazole condenses with benzaldehyde to *cinnamyl tolimidazole*, $C_7H_6 \langle{}^{N=}_{NH}\rangle C . CH : CH . C_6H_5$, and with phthalic anhydride to a *phthalone* (compare quinophthalone), which is oxidized by potassium permanganate to *tolimidazole-μ-carboxylic acid*, $C_8H_7N_2 . COOH$. Compare B. **25**, 2712, upon *polymeric* benzimidazoles.

Bisbenzimidazoles are made by reducing the o-nitro-oxanilides (A. **209**, 257):

$$C_6H_4 \langle{}^{NH-CO-CO-NH}_{NO_2} \quad {}_{O_2N}\rangle C_6H_4 \xrightarrow{H} C_6H_4 \langle{}^{N}_{NH}\rangle C-C \langle{}^{N}_{NH}\rangle C_6H_4.$$

Bisbenzimidazole, m. p. above 300°.

Benzobisimidazoles are formed from the o-diamidobenzimidazoles and carboxylic acids (B. **22**, 1652):

$$CH_3 . C \langle{}^{N}_{NH}\rangle C_6H_2 \langle{}^{NH_2}_{NH_2} + CH_3.COOH \longrightarrow CH_3 . C \langle{}^{N}_{NH}\rangle C_6H_2 \langle{}^{N}_{NH}\rangle C.CH_3$$

o-Diamidobenzo-*μ*-methylimidazole — Benzobis-*μ*-methylimidazole, m. p. 145°.

Benzimidazole hydrides, benzimidazolines, are not known with certainty. The primary products resulting from the interaction of monoalkylic o-diamines and aldehydes are considered as such. They give up hydrogen and readily change to benzimidazoles (B. **25**, 2827). The condensation products of acetoacetic ester with o-tolylenediamine (B. **25**, 606) behave similarly. Methylene iodide and dibenzene-sulphon-o-phenylenediamine yield **dibenzenesulphonmethylene-o-phenylenediamine**, $C_6H_4 < {}^{N(SO_2C_6H_5)}_{N(SO_2C_6H_5)} > CH_2$, melting at 148°. It can be considered as a derivative of the simplest benzimidazoline. In an attempt to split off the benzene sulphon-groups with hydrochloric acid it was resinified (B. **28**, R. 756).

These substances can be considered as derivatives of hydrobenzimidazoles, which result in the moderated reduction of acidylated o-nitranilines with ammonium sulphide (B. **22**, 1396):

$$C_7H_6 \langle{}^{NH . COCH_3}_{NO_2} \xrightarrow{H} C_7H_6 \langle{}^{NH}_{N-O}\rangle C . CH_3 \quad (\text{or } C_7H_6 \langle{}^{N=}_{N(OH)}\rangle C . CH_3)$$

Acet-o-nitrotoluide — Oxy-*μ*-methyl Tolimidazole.

These are relatively stable bodies, which yield benzimidazoles when they are distilled with zinc-dust.

The cyclic phenylene ureas, -thioureas, and -guanidines are *keto-*, *thio-*, and *imidobenzimidazolines*, which result from o-diamines with $COCl_2$ and $CSCl_2$ or CS_2, with urea and thiourea or ammonium sulphocyanide, with phenyl mustard oil and carbodiimide (p. 95):

$$C_6H_4<\substack{NH_2\\NH_2} + COCl_2\ (\text{or } CSCl_2) \longrightarrow C_6H_4<\substack{NH\\NH}>CO\ (\text{or } C_6H_4<\substack{NH\\NH}>CS)$$

$$C_6H_4<\substack{NH_2\\NH_2} + C(NC_6H_5)_2 \longrightarrow C_6H_4<\substack{NH\\NH}>C:NC_6H_5$$

Carbodiphenylimide — Phenylenephenyl Guanidine.

In many respects these bodies behave like oxy-, sulpho-, hydro-, and amido-derivatives of benzimidazoles, and permit a choice from the two formulas:

$$\text{I. } C_6H_4<\substack{NH\\NH}>CO(S.NH) \qquad \text{II. } C_6H_4<\substack{N=\\NH}>C.OH(SH, NH_2).$$

o-Phenylene Urea, *Benzimidazolon*, $C_6H_4(N_2H_2CO)$, melting at 308°, is also obtained from o-amidophenylurethane (B. **12**, 1296; **23**, 1047). **o-Toluylene Urea**, $C_7H_6(N_2H_2)CO$, melting at 290°, also results in the saponification of *μ-ethoxytolimidazole*, $C_7H_6(N_2H):C(OC_2H_5)$, melting at 163°. The latter is the reaction product of imidocarbonic ester and o-toluylenediamine.

o-Phenylenesulpho-urea, *Thiobenzimidazoline*, $C_6H_4(N_2H_2)CS$, melting at 298° with decomposition, is obtained from phenylenediamine sulphocyanide (A. **221**, 9; **228**, 244).

o-Phenylene-phenyl Guanidine, *μ-Anilidobenzimidazoline*, $C_6H_4(CN_3H_2C_6H_5)$, melting at 188°, is obtained from carbodiphenylimide and o-phenylenediamine.

The *oxazoles* and *thiazoles* correspond to the *imidazoles*. The latter were regarded as cyclic amidines (p. 495), and the former may be looked upon as cyclic imido-ethers and alkylene thioamides (1, 269). As a rule, these bodies are as little changed by reduction to hydride bases as the glyoxalines or imidazoles; they remain unaltered or are decomposed (comp. B. **29**, 2381).

7. OXAZOLES OR FURO-[b]-MONAZOLES.

The *oxazoles* or *furo-*[b]*-monazoles*, $\begin{matrix} N=\overset{\mu}{C}H \\ | \\ \underset{\beta}{C}H-\underset{\alpha}{C}H \end{matrix}>O$, are isomeric with the isoxazoles (furo-[a]-monazolon, p. 493). Oxazoles are produced (1) by the condensation of α-haloid ketones with acid-amides (B. **20**, 2576; **21**, 2195):

$$\begin{matrix} C_6H_5CO \\ | \\ CH_2Br \end{matrix} + \begin{matrix} NH_2 \\ O \end{matrix}\!\!>C.CH_3 \longrightarrow \begin{matrix} C_6H_5C-N \\ \| \\ CH-O \end{matrix}\!\!>C.CH_3\ .$$

β-Phenyl-μ-methyl Oxazole.

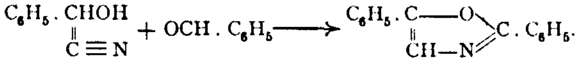
It may be assumed that here the ketone and amide react in the hydroxyl form.

(2) When concentrated sulphuric acid acts upon benzoïn and acid nitriles (B. **26**, R. 496):

$$\begin{matrix} C_6H_5.CO \\ | \\ C_6H_5.CH.OH \end{matrix} + N\equiv C.CH_3 \longrightarrow \begin{matrix} C_6H_5C-N \\ \| \\ C_6H_5CH-O \end{matrix}\!\!>C.CH_3$$

Benzoïn — α,β-Diphenyl-μ-methyloxazole.

(3) When hydrochloric acid gas acts upon mandelo-nitrile (and homologues) and benzaldehydes (B. **29**, 2097):

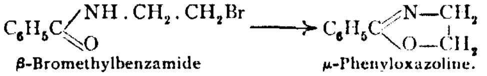


The oxazoles are feeble bases. They break down into acids and amines on evaporation with hydrochloric acid. Oxidants and reducing agents frequently rupture the oxazole ring with great ease. The parent substance of the group is not known.

β-Phenyl Oxazole, $C_3H_2(C_6H_5)NO$, melting at 46° and boiling at 222°, is made from formamide and bromacetophenone. **β-Phenyl-** and **α,β-Diphenyl-μ-methyl Oxazole,** melting at 45° and boiling at 242°, and melting at 44° and boiling at 192–195° (15 mm.); see above. **α-Methyl-μ-phenyl Oxazole,** from benzamide and chloracetone, is converted by alcoholic ammonia into *phenylmethyl glyoxaline*.

α,μ-Diphenyl Oxazole, melting at 74° and boiling above 360°, is formed from benzamide and phenylbromacetaldehyde by method 1, and, together with benzalmandelic amide, from the nitrile of mandelic acid and benzaldehyde by method 3 (B. **29**, 205). Chromic acid oxidizes it to *phenylglyoxylbenzamide*, $C_6H_5CO.CO.NH.CO.C_6H_5$, while sodium and alcohol reduce it to *benzylphenyloxethylamine*, $C_6H_5CH_2.NH.CH_2.CH(OH)C_6H_5$. Nitric acid apparently produces a nitrodiphenyl oxazole. It is converted into diphenylimidazole when heated with ammonia.

Dihydro-oxazoles, oxazolines, are produced by the condensation of β-haloid alkylamides with alkali (B. **22**, 2220):



β-Bromethylbenzamide μ-Phenyloxazoline.

μ-Phenyloxazoline, boiling at 243°, is broken down, in the reduction with sodium and amyl alcohol, to oxethylbenzylamine, $OHCH_2.CH_2.NHCH_2C_6H_5$ (B. **29**, 2382).

μ-Methyl Oxazoline is an oil. Its *picrate* melts at 159° (B. **23**, 2502).

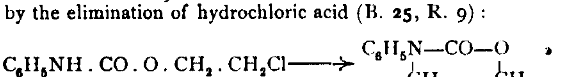
β-Methyl-μ-phenyl Oxazoline, boiling at 244°, is obtained from β-brompropylbenzamide, also from allylbenzamide, $C_6H_5.CO.NH.CH_2.CH:CH_2$, with concentrated sulphuric acid (B. **26**, 2840) (compare glyoxalidines, p. 499).

Amido-oxazolines or *imidotetrahydro-oxazoles* are the so-called allylene ψ-ureas.

Ethylene-ψ-urea, *μ-amido-oxazoline*, $\begin{matrix}CH_2-N\\ |\\ CH_2-O\end{matrix}\!\!>C.CH_3$; its *picrate* melts at 158°.

Propylene-ψ-urea, *μ-amido-α-methyl oxazoline*; its *picrate* melts at 186°. These compounds result from the action of potassium cyanate upon β-bromethyl- and -propylamine. **α,β-Diphenyl-μ-amidoxazoline,** melting at 154°, is formed from diphenyloxethylamine (p. 372) and potassium cyanate (B. **28**, 1899).

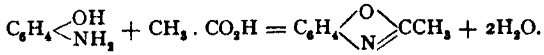
Derivatives of a ***ketotetrahydro-oxazole*** have been obtained from carbamic-β-haloid alkyl esters by the elimination of hydrochloric acid (B. **25**, R. 9):



Phenylcarbamic Chlorethyl Ester n-Phenyl-μ-ketotetrahydro-oxazole.

8. BENZOXAZOLES.

These, like the production of benzimidazoles from o-phenylene diamines, result upon heating o-amidophenols with carboxylic acids (p. 153):



o-Amidophenol μ-Methylbenzoxazole.

The benzoxazoles, also called alkenylamidophenols, are weak bases. They are resolved into their components on digesting them with acids. Some benzoxazole derivatives are substantive cotton dyes (B. **28**, 1127).

Benzoxazole, *Methenylamidophenol,* $C_6H_4\langle{}^{O}_{N}\rangle CH$, melts at 31° and boils at 183°.

μ-**Methyl Benzoxazole,** *ethenyl amidophenol,* boils at 201°. μ-**Phenyl Benzoxazole,** melting at 103°, is also formed in the reduction of benzoyl-o-nitrophenol (B. **9**, 1526; **29**, R. 358; A. **210**, 384).

μ-**Amidophenyl Toluoxazole,** $CH_3.C_6H_3\langle{}^{N}_{O}\rangle C.C_6H_4NH_2$, melting at 188°, is produced in the reduction of p-nitrobenzoyl-m-nitro-p-cresol. By combination of its diazo-derivative with β-naphthol, etc., carmine-red, acid-stable substantive cotton dyes are produced.

Oxy- and *thio*-derivatives of the benzoxazoles are obtained from o-amidophenols with $COCl_2$ or $ClCO_2R$ and CS_2 or $CSCl_2$. *Amido*-derivatives result on heating thio- or oxy-compounds with amines. Here, as in the case of analogous benzimidazole compounds, two formulas may be considered for these bodies:

$C_6H_4\langle{}^{O}_{N}\rangle C(OH)$	$C_6H_4\langle{}^{O}_{N}\rangle C(SH)$	$C_6H_4\langle{}^{O}_{N}\rangle C(NH_2)$
$C_6H_4<{}^{O}_{NH}>CO$	$C_6H_4<{}^{O}_{NH}>C:S$	$C_6H_4<{}^{O}_{NH}>C:NH$
μ-Oxybenzoxazole	μ-Thiobenzoxazole	μ-Amidobenzoxazole.

Isomeric alkyl compounds are derived from the two forms of μ-oxybenzoxazole, which may be distinguished as *lactime* and *lactam ethers* or O- and N-alkyl derivatives. The amidobenzoxazoles exhibit similar conditions.

μ-**Oxybenzoxazole,** *Carbonyl Amidophenol,* $C_7H_5NO_2$, melting at 137°, is insoluble in alkalies. Methyl iodide converts it into an n-ethyl derivative.

n-**Ethyl Benzoxazolon,** $C_6H_4<{}^{O}_{N(C_2H_5)}>CO$, melts at 29°. μ-**Ethoxybenzoxazole,** $C_6H_4\langle{}^{O}_{N}\rangle COC_2H_5$, is formed from imidocarbonic ester and o-amidophenol (B. **19**, 2655). μ-**Thiobenzoxazole,** C_7H_5NSO, *melting at 193–196°, is soluble in alkalies* and ammonia. It is obtained from amidophenol hydrochloride by the action of potassium xanthogenate; also from o-oxyazobenzene and CS_2.

μ-**Anilidobenzoxazole,** $C_7H_5N_2O(C_6H_5)$, melting at 137°, is produced simultaneously. The latter is also formed on heating thiobenzoxazole with aniline. μ-**Amidobenzoxazole,** $C_7H_6N_2O$, melting at 130°, is isomeric with o-phenylene urea (p. 502). It results on splitting off hydrogen sulphide from o-oxyphenylsulphourea by means of mercuric oxide. μ-**Phenylimido-n-ethylbenzoxazolon,** $C_6H_4<{}^{O}_{N(C_2H_5)}>C:N.C_6H_5$, is formed from n-ethyl benzoxazolon and aniline (J. pr. Ch. [2], **42**, 450).

9. THIAZOLES OR THIO-[b]-MONAZOLES.

Just as the oxazoles are prepared from acid-amides, so the thiazoles or *thio*-[b]-*monazoles,*

$$\begin{matrix} & (\mu) \\ N & = CH \\ | & \\ CH & = CH \\ (\beta) & (\alpha) \end{matrix}>S,$$

are obtained from the thio-amides and α-haloid ketone derivatives:

$$\underset{\text{Chloraldehyde}}{\begin{matrix} HC:O \\ | \\ H_2CCl \end{matrix}} + \underset{\text{Thiacetamide}}{\begin{matrix} HN \\ HS \end{matrix}>C.CH_3} \longrightarrow \underset{\mu\text{-Methyl Thiazole.}}{\begin{matrix} HC-N \\ \| \\ HC-S \end{matrix}>C.CH_3}$$

Further, thiazole and its homologues result from the action of nitrous acid and alcohol upon μ-amidothiazoles just as the benzene hydrocarbons are obtained from the anilines.

Behavior: Thiazole may be derived from pyridine, just as thiophene is derived from benzene—*i. e.*, by imagining a CH : CH-group replaced by sulphur. Accordingly, the thiazoles show a like agreement or similarity in their physical and in part in their chemical properties with the pyridines, just as the thiophenes do with the benzenes.

The thiazoles are tertiary bases, forming addition-products with alkyl iodides. As a rule, they are stable toward oxidizing agents; chloric acid, however, destroys them.

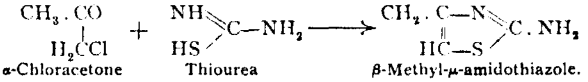
Thiazole, C_3H_3NS, boiling at 117°, has an odor like that of pyridine. It results when N_2O_3 and alcohol act upon μ-amido-thiazole. $C_3H_3NS.HCl.AuCl_3$ melts with decomposition at 248–250°. $C_3H_3NS.HgCl_2$ melts at 202–204°. **α-Methyl Thiazole,** $C_3H_2(CH_3)NS$, boiling at 232°, is obtained from its amido-compound and by distilling methyl oxythiazole with zinc-dust (A. **250**, 279). The isomeric **μ-methyl thiazole,** boiling at 128°, with an odor like picoline (see this), is prepared from monochloracetone and thiacetamide. **α,μ-Dimethyl Thiazole,** boiling at 143°, from chloracetone and thiacetamide, when reduced by sodium and alcohol is resolved into ethyl propylamine and hydrogen sulphide. It condenses, like the α-methylated pyridines, with formic aldehyde to an alkine, $C_3HNS(CH_3)(CH_2.CH_2OH)$ (B. **27**, 1009).

Trimethyl Thiazole, $C_3(CH_3)_3NS$, melts at 167°. **α-Phenyl Thiazole** melts at 52° and boils at 273°. **Triphenyl Thiazole,** melting at 87°, is formed from thiobenzamide and bromdesoxybenzoïn or desylbromide.

Haloid thiazoles are prepared by acting with concentrated haloid acids upon diazothiazoles:

μ-Chlorthiazole boils at 145° and **μ-bromthiazole** boils at 171°.

μ-Amidothiazoles result from the action of α-haloid keto-compounds upon thioureas:



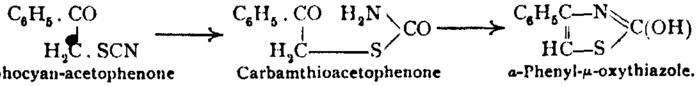
α-Chloracetone   Thiourea   β-Methyl-μ-amidothiazole.

Substances are formed from the symmetrical dialkylic thioureas which are derived from *imidothiazoline.* Consult A. **265**, 110, for isomeric monalkylamidothiazoles.

The amidothiazoles are similar to the anilines. They can be converted into diazo-compounds, and through these into haloid thiazoles, thiazoles, thiazole-azo-dyes, etc.

μ-Amido-thiazole, $C_3H_2(NH_2)NS$, melting at 90°, may be prepared from dichlorether and thiourea. Its *nitrate* is converted by N_2O_3 into **Diazothiazole Hydrate,** $C_3H_2(.N:NOH)NS$, which yields yellow to brown-colored azo-dyes with resorcinol, naphthol, etc. (A. **246**, 40). **Methyl-μ-amido-thiazole,** $C_3H(CH_3)(NH_2)NS$, melting at 42° and boiling at 136° (30–40 mm.), is formed from chloracetone and thiourea or ammonium sulphocyanide (B. **20**, 3127). **Phenyl-μ-amidothiazole,** $C_3H(C_6H_5)(NH_2)NS$, from ω-chloracetophenone (p. 231), yields *phenyldiazothiazole hydrate* (A. **261**, 14). **β,n-Dimethyl-μ-methyl Imidothiazoline,** $\begin{matrix} HC - S \\ \| \\ CH_3C - N.CH_3 \end{matrix} \!\!>\! C:NCH_3$, melting at 96°, is obtained from chloracetone and symmetrical dimethyl thiourea.

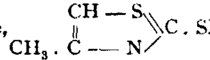
Oxythiazoles are obtained from α-sulphocyan-ketones by the action of alkali:



Sulphocyan-acetophenone   Carbamthioacetophenone   α-Phenyl-μ-oxythiazole.

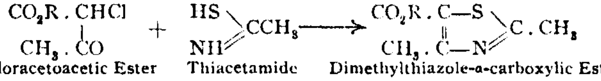
β-Methyl-μ-oxythiázole, $C_3H(CH_3)(OH)NS$, melting at 160°, results from the exit of carbon dioxide from its carboxylic acid and also when alkalies act upon sulphocyan-acetone (A. **259**, 297; B. **25**, 3652). **α-Phenyl-μ-oxythiazole** melts at 204° (A. **249**, 16) (see above).

Mercaptothiazoles result upon heating α-chlorketones with ammonium dithiocarbaminate:

β-Methyl-μ-mercapto-thiazole,  melts at 90°.

β-Phenylmercapto-thiazole melts at 168° (B. **26**, 604).

Thiazole Carboxylic Acids: Their esters are produced in the condensation of chloracetoacetic ester, chloroxalo-acetic ester, etc., with thioamides:



α-Chloracetoacetic Ester   Thiacetamide   Dimethylthiazole-α-carboxylic Ester.

Furthermore, the *amido-*, *oxy-*, and *mercapto-thiazole* carboxylic acids are formed by reactions similar to those employed for the amido-, oxy-, and mercapto-thiazoles, if instead of the ketone derivatives the corresponding ketone carboxylic acids are introduced into the reactions.

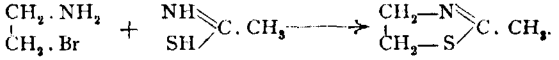
β-Methylthiazole-α-carboxylic Acid, $C_3(CH_3)HNS(COOH)$, melts at 257°. Its ester is obtained from amidomethylthiazole carboxylic ester (see below) by converting it into chlorthiazolecarboxylic ester and then reducing the latter.

μ-Methyl-α,β-thiazole Dicarboxylic Acid, $C_3(CH_3)(COOH)_2NS$, melts with decomposition at 169°. It is formed from chloroxaloacetic ester and thiacetamide. **μ-Methyl-β-thiazylacetic Ester,** $C_3H(CH_3)(CH_2.CO_2R)NS$, boiling at 239°, is formed from γ-bromacetoacetic ester and thiacetamide.

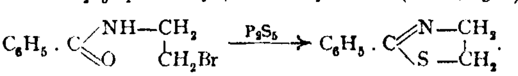
μ-Amidothiazole-β-carboxylic Acid, Sulphuvinic Acid, $C_3HSN(NH_2)COOH$ (+ $2H_2O$), decomposes at 245°, and is formed from dibrompyroracemic acid. Its *ester*, melting at 173°, is produced from monobrompyroracemic ester and thiourea (A. **261**, 25).

μ-Amido-methylthiazole-β-carboxylic Ester, melting at 175°, is obtained from α-chloracetoacetic ester and thiourea. Its *diazohydrate* melts at 100° with decomposition. **μ-Oxy-β-methylthiazole Carboxylic Ester,** $C_3(OH)(CH_3)SN.COOC_2H_5$, melting at 128°, is formed from α-sulphocyanacetoacetic ester (A. **259**, 284, 298). **μ-Mercapto-β-methylthiazole Carboxylic Ester,** $C_3(SH)(CH_3)SN.COOC_2H_5$, melting at 141°, is formed from α chloracetoacetic ester and ammonium dithiocarbaminate (B. **26**, R. 604).

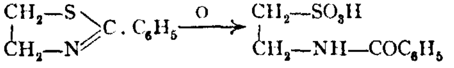
Dihydrothiazoles or *thiazolines* are synthesized from (1) alkylen haloids, or β-haloid alkylamines and thioamides (B. **24**, 783; **29**, 2610):

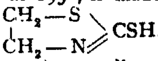


(2) By the action of P_2S_5 upon acidyl-β-bromalkylamides (B. **26**, 1328):



The thiazolines are much more readily decomposed than the thiazoles. **μ-Methyl Thiazoline,** boiling at 145°, on evaporation with hydrochloric acid, becomes β-amidoethyl mercaptan. **μ-Phenylthiazoline,** boiling at 276°, is obtained from benzoyl-β-bromethylamide by the action of P_2S_5. It yields benzoyl taurine when it is oxidized:

 (B. **23**, 158).

α-Methyl-μ-tolylthiazoline, $C_3H_3(CH_3)(C_7H_7)NS$, boiling at 295°, is made from β-brompropyltolylamide and P_2S_5. **Thiazoline-μ-mercaptan,** , melting at 107°, is prepared from bromethylamine and S_2C (B. **22**, 1152), as well as by the action of carbon bisulphide upon vinylamine, $CH_2:CH.NH_2$ (B. **28**, 2932).

The alkylen derivatives of pseudosulphourea, previously discussed, are *amidothiazolines*. They have mostly been obtained by rearrangement of allyl thioureas (*thiosin-*

amines, I, 409) : μ-**Anilido-α-methyl Thiazoline**, n-*Phenylpropylene-ψ-thiourea*, $C_3H_3(CH_3)NS(NHC_6H_5)$, melting at 117°, is made from allyl phenylthiourea :

$$\begin{array}{l} CH_2=CH \quad HS \\ \quad\quad\quad\quad\quad\quad > CNHC_6H_5 \text{ (B. 22, 2991).} \\ CH_2 - N \end{array}$$

μ-**Piperyl-α-methyl Thiazoline**, $C_3H_3(CH_3)NS(NC_5H_{10})$, boiling at 277°, is obtained from allylpiperylthiourea (B. 24, 265). μ-**Methylamido-α,β-diphenylthiazoline**, $C_3H_2(C_6H_5)_2NS(NHCH_3)$, melting at 155°, is derived from diphenyloxyethylamine (p. 372) and methyl mustard oil (B. 28, 1900).

The following are derivatives of tetrahydrothiazole:

β,μ-**Diketotetrahydrothiazole, or Mustard Oil Acetic Acid**, $\begin{array}{l} CH_2 - S \\ | \quad\quad\quad > CO, \\ CO - NH \end{array}$ melting at 112°. It results on evaporating sulphocyanacetic acid or sulphocyanacetamide with acids (B. 26, R. 324; I, 423).

β,μ-**Ketoïmidotetrahydrothiazole**, $\begin{array}{l} CH_2 - S \\ | \quad\quad\quad > CNH, \\ CO - CH_2 \end{array}$ melting at 71°, is formed in the action of concentrated sulphuric acid upon sulphocyanacetamide. β,μ-**Diketotetrahydrothiazole Acetic Acid**, $\begin{array}{l} COOH\,.\,CH_2\,.\,CH - S \\ \quad\quad\quad\quad\quad | \quad\quad\quad > C : NH, \\ \quad\quad\quad\quad OC - NH \end{array}$ melting with decomposition at 169°, is formed from β,μ-**imidoketotetrahydrothiazole acetic acid**, $\begin{array}{l} COOH\,.\,CH_2\,.\,CH - S \\ \quad\quad\quad\quad\quad | \quad\quad\quad > C : NH, \\ \quad\quad\quad\quad OC - NH \end{array}$ melting at 216°, which is the condensation product of chlorsuccinic acid and thiourea (B. 27, R. 742).

10. BENZOTHIAZOLES.

The benzothiazoles, the analogues of the benzimidazoles and benzoxazoles (*anhydro-bases*) are prepared (1) from o-amidothiophenols (p. 157) and carboxylic acids (their chlorides or anhydrides) by the exit of water (A. W. Hofmann, B. 13, 1224):

$$C_6H_4{<}^{SH}_{NH_2} + COOHR \longrightarrow C_6H_4{<}^{S}_{N}{>}C.R.$$

(2) Upon heating acid anilides with sulphur, or oxidizing thioanilides with potassium ferricyanide:

$$\begin{array}{c} C_6H_5-N \\ \quad\quad\quad > C.C_6H_5 \\ HS \end{array} \xrightarrow{O} C_6H_4{<}^{N}_{S}{>}C.C_6H_5$$

Thiobenzanilide · μ-Phenylbenzothiazole.

Phenylbenzothiazole is also produced on heating benzylamine with sulphur. Hydrogen sulphide is evolved and thiobenzanilide is first formed, which then reacts in the sense above indicated (A. 259, 300).

The benzothiazoles are feeble bases; their odor resembles that of quinoline. Fusion with caustic potash resolves them into amidothiophenols and carboxylic acids.

Different benzothiazole derivatives are important as *substantive cotton dyes*.

Benzothiazole, *Methenyl amidothiophenol*, $C_6H_4(NSCH)$, boiling at 234°, is produced from o-amidothiophenol and formic acid, or formanilide and sulphur.

Benzisothiazole, $C_6H_4{<}\begin{smallmatrix} CH \\ | \\ N \end{smallmatrix}{>}S$, boiling at 242°, is isomeric with benzothiazole. It is formed in the reduction of the o-nitrobenzyl ester of carbaminthiolic acid or of o-nitrobenzylmercaptan (p. 180) (B. 28, 1028; 29, 160). μ-**Methylbenzothiazole**, $C_6H_4(NSC_2H_3)$, boils at 238°. μ-**Phenylbenzothiazole** melts at 114°. μ,p-**Amidophenyl-toluthiazole, Dehydrothiotoluidine**, $CH_3\,.\,C_6H_3{<}^{N}_{S}{>}C\,.\,C_6H_4\,.\,NH_2$, melt-

ing at 191°, is produced when thiotoluidine is heated with sulphur. Its *trimethylammonium chloride* derivative is the dye **Thioflavin.** Dehydrotoluidine, when further heated with thiotoluidine and sulphur, yields the base of the dye **Primulin**:

$$CH_3 . C_6H_3\left\langle{}^{S}_{N}\right\rangle C . C_6H_3\left\langle{}^{S}_{N}\right\rangle C . C_6H_4NH_2.$$

A series of benzothiazole derivatives has been obtained from **chlorphenyl-mustard oil,** or μ-**chlorbenzothiazole,** $C_6H_4\left\langle{}^{S}_{N}\right\rangle CCl$, melting at 24° and boiling at 248°. It results when PCl_5 acts upon phenyl-mustard oil. The reduction of chlorphenyl-mustard oil leads to benzothiazole; with alcohol we get μ-oxybenzothiazole; with sodium ethylate, μ-ethoxybenzothiazole; with sodium sulphydrate, sulphydro-, with ammonia, amido-, and with aniline, anilido-benzothiazole. μ-**Oxybenzothiazole,** $C_6H_4(NSC\text{-}OH)$, melting at 136°, is formed from chlorcarbonic ester and amidothiophenol. μ-**Ethoxybenzothiazole,** *ethoxy-mustard oil*, $C_6H_4(NSCO_2H_5)$, melting at 25° and boiling above 360°, results upon oxidizing phenylthiomethane with potassium ferricyanide.

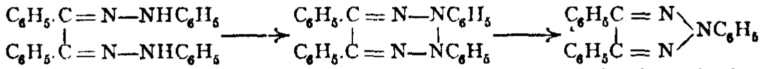
μ-**Sulphydrobenzothiazole,** $C_6H_4(NSC . SH)$, melting at 179°, is also obtained from amidothiophenol and CS_2; from azobenzene with CS_2; from phenyl-mustard oil and sulphur, etc. (B. 24, 1403). μ-**Amidobenzothiazole,** $C_6H_4(NSC . NH_2)$, melts at 129° (B. 13, 11). μ-**Anilidobenzothiazole,** $C_6H_4(NSC . NHC_6H_5)$, melting at 159°, is also formed from azobenzene and phenyl-mustard oil (B. 24, 1410). **Bis-benzothiazole,** $C_6H_4\left\langle{}^{N}_{S}\right\rangle C . C\left\langle{}^{N}_{S}\right\rangle C_6H_4$ (B. 29, R. 87), is produced when sulphur is heated with acetanilide.

The hypothetical nucleus of **Selenazole,** $\begin{matrix} N = CH \\ | \\ CH = CH \end{matrix}\!\!>\!Se$, corresponds to thiazole. Some derivatives of it have been obtained in a manner similar to that used with the analogous thiazole derivatives. μ-**Methyl Selenazoline,** $\begin{matrix} N = C(CH_3) \\ | \\ CH_2 - CH_2 \end{matrix}\!\!>\!Se$, boiling at 161°, results on treating di-acetamidoethyldiselenide, $(CH_3 . CO . NH . CH_2 . CH_2Se)_2$, with phosphorus pentachloride. It is an oil with an odor resembling that of pyridine (B. 25, 3048). μ-**Imidotetrahydroselenazole,** *Ethylene-ψ-selenurea*, $\begin{matrix} NH - C(NH) \\ | \\ CH_2 - CH_2 \end{matrix}\!\!>\!Se$, is an oil. It is obtained from bromethylamine and potassium selenocyanide (B. 23, 1003). The ring-homologous trimethylene-ψ-selenurea, $\begin{matrix} CH_2 - NH - C : NH \\ | \qquad\qquad | \\ CH_2 - CH_2 - Se \end{matrix}$, is prepared in an analogous way.

II. OSOTRIAZOLES OR PYRRO-[aa₁]-DIAZOLES.

Osotriazones (1, 328), *pyrro-[aa_1]-diazoles,* $\begin{matrix} CH = N \\ | \\ CH = N \end{matrix}\!\!>\!NH$, derivatives of osotriazole, are formed:

1. By boiling with acids or distilling the osazones of o-diketo-compounds, or the osotetrazones, which are the oxidation products of the osazones:



Benzil Osazone — Benzil Osotetrazone — Triphenyl Osotriazole.

2. By the action of acetic anhydride or PCl_5 upon the hydrazoximes of the o-diketo-compounds; water is split off in this reaction (p. 124):

$$\begin{array}{l} C_6H_5—C=NNHC_6H_5 \\ \quad\;\; | \\ C_6H_5—C=NOH \end{array} \longrightarrow \begin{array}{l} C_6H_5C=N \\ \quad\;\; | \\ C_6H_5C=N \end{array}\!\!>N.C_6H_5.$$

The methyl phenylhydrazones of α-ketoximes also yield osotriazoles with the elimination of methyl alcohol (Pechmann, A. **262**, 265).

Behavior: Osotriazoles are mostly feeble basic liquids with an odor resembling the alkaloids. They distil without decomposition. Their imide hydrogen can be replaced by metals. The phenyl group of the n-phenyltriazoles can be split off after amidation by simple oxidation. Potassium permanganate oxidizes c-alkylosotriazoles to osotriazole carboxylic acids. However, the osotriazole ring is stable toward most reagents.

Osotriazole, $C_2H_3N_3$, melting at 22° and boiling at 204°, is obtained from its carboxylic acid (see below). Silver nitrate precipitates *osotriazole silver*, $C_2H_2N_3Ag$, from its aqueous solution. Benzoyl chloride produces n-*benzoyl osotriazole*, melting at 100°. n-**Phenylosotriazole,** $C_2H_2N_3.C_6H_5$, boiling at 224°, is formed from its carboxylic acid or from glyoxal osotetrazone. n-**Phenylmethylosotriazole,** $C_2H(CH_3)N_3.C_6H_5$, boiling at 150° (60 mm.), is obtained from methyl glyoxal. n-**Phenyldimethylosotriazole,** $C_2(CH_3)_2N_3.C_6H_5$, boiling at 192° (60 mm.), is formed from dimethyl glyoxal (I, 328; II, 124). **Triphenylosotriazole,** $C_2(C_6H_5)_3N_3$, melting at 122°, is obtained from benzil (B. **21**, 2806).

n-**Phenyl-c-amido-c-methylisotriazole,** $C_2(CH_3)(NH_2)N_3C_6H_5$, melting at 83°, is formed from acetylamidrazonphenylhydrazone, $C_6H_5NHN:C(NH_2).C(CH_3):N.-NHC_6H_5$ (B. **26**, 2783; **28**, 1283). It forms a *diazo compound*, which, on boiling with water, becomes **n-phenylmethyl oxyosotriazole,** $C_2(CH_3)(OH)N_3C_6H_5$, melting at 141°, and with potassio-copper cyanide it forms n-*phenylmethylcyantriazole*.

n-**Phenyldiamido-osotriazole,** $C_2N_3(C_6H_5)(NH_2)_2$, melting at 143°, is derived from oxalenphenylhydrazide-amidoxime, $C_6H_5NH.N:C(NH_2)C(NH_2):NOH$. In certain respects it shows great similarity to the aromatic o-diamines (p. 95), in that it forms an *azine*-like blue dyestuff; with o-diketones it yields *quinoxaline*-like bodies. It does not form *anhydro*-bases. Nitrous acid converts it into a stable *diazo*-compound, which is readily changed by sodium acetate to *phenylosotriazole-azimide*,

$$C_6H_5N\!\!<\!\begin{array}{l} N=C—NH \\ \quad\;\;\; | \\ N=C—N \end{array}\!\!>N.$$ The latter can be readily decomposed into the diazo-compound (A. **295**, 129).

n-**Phenyltriazole Aldehyde,** $C_2H(CHO)N_3C_6H_5$, melting at 70°, is obtained from its *oxime*, melting at 115°, which is formed from diisonitrosoacetone phenylhydrazone, $\begin{array}{l} HON:CH.C=N.NHC_6H_5 \\ \qquad\quad\;\, | \\ \qquad\quad CH=N.OH \end{array}$ (I, 479). By the exit of water the aldoxime becomes n-*phenylcyantriazole*, $C(CN)HN_3C_6H_5$, melting at 94°.

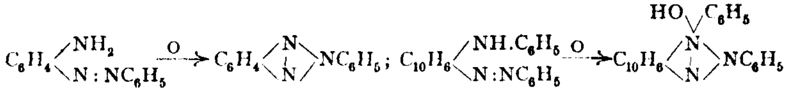
Osotriazole Carboxylic Acid, $C_2(COOH)HN_3H$, melting at 211°, results in the oxidation of n-*amidophenylosotriazole carboxylic acid* with potassium permanganate. The latter acid is obtained by the amidation of **n-phenylosotriazole carboxylic acid,** $C_2(COOH)HN_3C_6H_5$, melting at 192°, the oxidation product of n-phenylmethyltriazole. Phenylosotriazole carboxylic acid, when reduced by sodium amalgam, is resolved into prussic acid and phenylhydrazido-acetic acid. n-**Phenylosotriazole Dicarboxylic Acid,** $C_2(COOH)_2N_3C_6H_5$, melting at 236°, from phenyldimethyltriazole, readily yields an *anhydride*, melting at 184°.

The **pseudo-azimides** may be viewed as benzo-derivatives of osotriazoles. A constitution similar to that given the indazoles has been ascribed to them, hence they may be called ***indiazoles:***

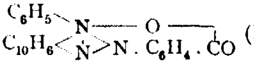
$C_6H_4\!<\!\begin{array}{c}CH\\N\end{array}\!>NR$	$C_6H_4\!<\!\begin{array}{c}N\\N\end{array}\!>NR$
Indazoles	Pseudoazimides.

Pseudoazimides are produced when o-amido-azo-compounds are oxidized (comp. B. **25**, 901; **27**, 2374, etc.). The condensation can also be effected by means of thionyl chloride (B. **28**, 2201).

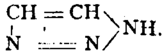
Should the amido-group be substituted the oxidation will give rise to ammonium hydroxide compounds (B. **20**, 1174; **28**, 328). Heretofore, such compounds were only prepared from bases of the naphthalene series. This reaction can easily be made retrogressive by reducing agents:



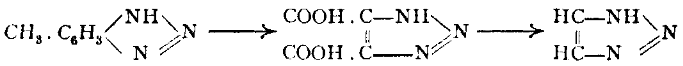
o-Amido-azobenzene — n-Phenyl-ψ-azimido-benzene, m. p. 109° — Benzene-azonaphthyl-aniline — Diphenyl-naphthalene Azoammonium Hydroxide.

o-Anilidonaphthalene-azo-benzoic acid yields the acid of the latter compound. It readily changes to a betaïne-like anhydride :  (B. **28**, 333).

12. PYRRO[ab]DIAZOLES:

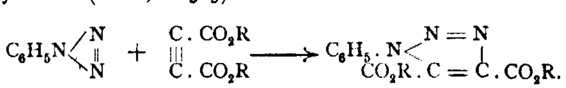


The azimides, or benzopyrro[ab]diazoles, are isomeric with the pseudoazimides. The oxidation of azimidotoluene produces pyrro[ab]diazole dicarboxylic acid, which by the loss of CO_2 becomes azole, the constitution of which is proved by this method of formation (B. **26**, 2736):



Azimido-toluene — Pyrrodiazole Dicarboxylic Acid — Pyrro[ab]diazole.

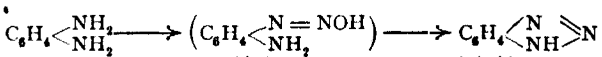
Pyrro[ab]diazole boils at 209°; its *benzoyl*-derivative melts at 111°. **Pyrro[ab]-diazole Dicarboxylic Acid** melts with decomposition at 200°. **n-Phenylpyrro[ab]-diazole Dicarboxylic Acid**, $C_2(COOH)_2N_3C_6H_5$, melting at 150°, is probably the acid, the *ester* (m. p. 127°) of which is produced when diazobenzene-imide acts upon acetylene dicarboxylic ester (B. **26**, R. 585):



This reaction is similar to that by which pyrazole carboxylic esters are formed from diazo-acetic with acetylene dicarboxylic esters (p. 485).

Consult J. pr. Ch. [2], 53, 341, for an n-oxypyrro[ab]diazole dicarboxylic acid.

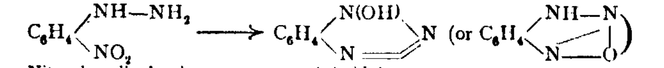
Benzopyrro[ab]diazoles or **azimide-benzenes** result from the action of nitrous acid upon o-diamines (p. 96):



o-Phenylenediamine — o-Amidodiazobenzene — Azimidobenzene.

When the benzene nucleus is substituted the n-substituted azimidobenzenes occur in two isomeric forms, determined by the position of the NR-group with reference to the benzene substituents. This is a proof of the unsymmetrical structure of the azimidobenzenes. When, however, the NH-group is free there always appears to be but one preferred position of the hydrogen atom (see uramidoazimidobenzoic acids, p. 212 and A. 291, 313). The azoïmidobenzenes no longer manifest the instability of the diazo- or diazamido-derivatives, but can be distilled without decomposition. The imide hydrogen can be replaced by alkyls. The tertiary bases form ammonium bases with alkyl iodides.

n-*Oxyderivatives* of the azimido-benzenes, the **Azimidoles,** are formed when alkalies act upon o-nitrophenylhydrazines (B. **27**, 3381; **29**, R. 790):



o-Nitrophenylhydrazine — Azimidole.

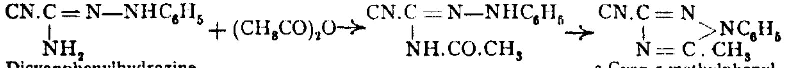
Azimido-benzene, $C_6H_4(N_3H)$, melting at 98°, is isomeric with diazobenzene-imide (p. 111). **[2]n-Phenylazimido[4]ethoxy-benzene** melts at 108°. **[2]n-Phenyl-azimido[5]ethoxy-benzene** melts at 99° (compare J. pr. Ch. [2], **53**, 97). **n-Tolyl-azimido-toluene,** $C_7H_6(N_3 . C_7H_7)$, melting at 95°, is derived from o-amidoditolylamine (B. **25**, 1023), and is isomeric with *n-tolyl ψ-azimido-toluene* (p. 510), melting at 126°.

Benzoazimidole, $C_6H_4(N_3OH)$, melting at 157°, is formed in the action of alkalies upon o nitrophenylhydrazine. It is a rather strong acid. It yields the iodethylate of n-ethylazimidobenzene with ethyl iodide. Hydriodic acid reduces it to azimidobenzene, while potassium permanganate oxidizes it to a strong tribasic acid, probably n-oxypyrro-[ab]diazole dicarboxylic acid (see above).

13. TRIAZOLES.

The triazoles or *pyrro-*[ab$_1$]*-diazoles*, (3)CH = N(2) / (4)N = CH(5) >NH(1), are isomeric with oso-triazole and pyrro[ab]-diazole. The symmetrical formula of a **pyrro-[bb$_1$] diazole,** N = CH / N = CH >NH, may be suggested for the simplest triazole; certain of the n-alkyl triazoles introduced here are derived from it. In behavior the triazoles recall the pyrazoles (p. 482).

Formation of Triazoles: (1) Cyantriazoles are formed when the anhydrides of fatty acids act upon dicyanphenylhydrazine or cyanamidrazone (B. **26**, 2385). Aldehydes and ketones react similarly (Bladin, B. **18**, 1544; **25**, 183):

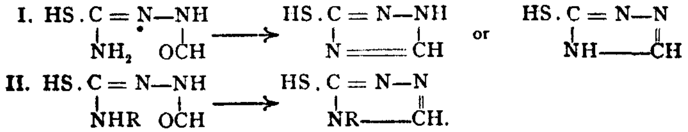


Dicyanphenylhydrazine — 3-Cyan-5-methylphenyl-triazole.

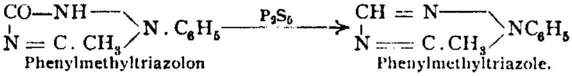
Acetylcyanamidrazone is an intermediate product. It may be viewed as a mono-hydrazone of a β-diketone, the terminal CH_2-group of which has been replaced by NH; this renders the reaction parallel with that of the formation of the pyrazoles from the hydrazones of the β-diketones.

Other *amidrazones* or *hydrazidines* (p. 129) (B. **27**, 3273)—*e. g.*, phenylamidrazone-methyl ketone (B. **26**, 2782), amidoguanidine (B. **26**, 2598), benzoylbenzenylhydrazidine (B. **27**, 989), etc.—react like cyanamidrazone.

(2) Acidylthiosemicarbazides of the general formula HS . C(NHR) : N . NHCOR, when heated beyond their melting point, yield mercaptotriazoles, which change to triazoles upon oxidation. The resulting triazole derivatives, so far as they are formed from n-alkylic thiosemicarbazides, are derived from a pyrro[bb$_1$]diazole (see above) (B. **29**, 2483):



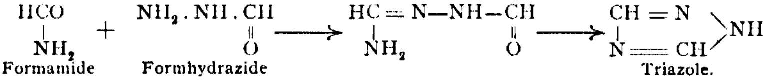
(3) **Triazoles result upon distilling triazolons and urazoles with P_2S_5 (see p. 481)** (B. **25**, 225; **27**, R. 408):



Phenylmethyltriazolon Phenylmethyltriazole.

The chlortriazoles formed by the action of PCl_5 upon the triazolons can be reduced to triazoles (below).

(4) The method of producing triazoles by the condensation of acid hydrazides with acid amides is very simple (B. **27**, R. 801). The reaction can be further simplified by allowing one molecule of hydrazine hydrochloride to act upon two molecules of the acid amide; the acid hydrazide will be formed in the first phase (Gaz. chim. ital. **26**, II, 413):



Formamide Formhydrazide Triazole.

Behavior: The triazoles, like the other pyrrodiazoles, are feebly basic, nearly neutral bodies. The **platinum chloride double salts** behave similarly to the pyrazoles (p. 481, Gaz. chim. ital. **26**, II, 417). The imide-hydrogen is replaceable by metals. c-Alkyltriazoles yield triazole carboxylic acids when they are oxidized. In the n-phenyl triazoles the phenyl group, particularly after amidation, is split off by oxidation (compare n-phenyl pyrazoles, n-phenyl osotriazoles, pp. 483, 508).

Triazole, $C_2H_3N_3$, melting at 121° and boiling at 260°, is obtained (1) from formamide and formhydrazide; (2) by distilling urazole with P_2S_5; (3) from its carboxylic acid; (4) in the oxidation of mercaptotriazole with hydrogen peroxide (B. **29**, 2485). **n-Methyl-** and **n-ethyl triazoles** are similarly formed from the corresponding mercaptan derivatives. **3-Methyl Triazole,** $C_2H_2(CH_3)N_3$, melting at 94°, is derived from n-phenyl-3-methyl triazole by elimination of the C_6H_5-group by the oxidation process (B. **25**, 225). **n-Phenyl Triazole,** $C_2H_2N_3C_6H_5$, melting at 47° and boiling at 266°, is derived from its carboxylic acid. **n-Phenyl-3-methyl Triazole,** $C_2H(CH_3)N_3C_6H_5$, melting at 87° and boiling at 274°, results when P_2S_5 acts upon n-phenylmethyl triazolon. Isomeric **1,5-Phenyl methyl triazole,** melting at 191°, is formed from its carboxylic acid. **1,5-Diphenyl triazole,** melting at 91°, is produced when 1,5-phenyl-3-chlortriazole is heated to 150–160° with phosphorus and hydriodic acid. **c-Diphenyl Triazole,** $C_2(C_6H_5)_2N_3H$, melting at 188°, is obtained from benzoylbenzenyl hydrazidine (p. 205). **c-Difuryl Triazole,** $C_2(C_4H_3O)_2N_3H$, melting at 185°, is formed when difurylhydrazidine, $C_4H_3O \cdot C\begin{matrix}\diagup NH_2 \quad HN \diagdown \\ \diagdown N —— NH \diagup\end{matrix}C \cdot C_4H_3O$, is boiled with glacial acetic acid (B. **28**, 465). **1,3,5-Triphenyl Triazole,** melting at 104°, is produced in the condensation of phenylhydrazine with benzonitrile in the presence of sodium (B. **29**, R. 1125).

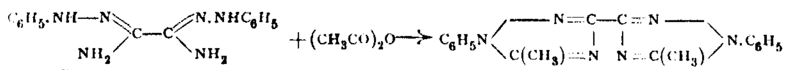
Chlortriazoles result on heating triazolons with PCl_5 and $POCl_3$ to elevated temperatures. The chlorine in them is intimately bound and can only be removed on heating with HI + P. **1-Phenyl-5-chlortriazole** melts at 54°. **1,5-Diphenyl-3-chlortriazole** melts at 96°, **1-Phenyl-3,5-dichlortriazole** melts at 94° (B. **29**, 2671; C. 1897, I, 857).

Mercaptotriazoles, from acidylthiosemicarbazides (see method 2), yield disulphides by gentle oxidation. More energetic oxidation splits off sulphur, and triazoles result. **Mercaptotriazole** melts at 216°. **n-Methyl** and **n-Ethyl Mercaptotriazole** melt at 168° and 97° (B. **29**, 2484).

5-Amido-3-methyl Triazole, $C_2(NH_2)(CH_3)N_3H$, melting at 148°, is obtained from acetylamidoguanidine, $NH_2 \cdot C\begin{matrix}\diagup NHNH_2 \\ \diagdown NH \cdot CO \cdot CH_3\end{matrix}$ (B. **26**, 2589). **3-Acetyl-1-phenyl-5-methyl Triazole,** $C_2(COCH_3)(CH_3)N_3C_6H_5$, melting at 89°, is derived from phenylamidrazon-methyl ketone (B. **26**, 2787). **3-Cyan-1-phenyl-5-methyl Triazole,** melting at 109°, is formed from dicyanphenylhydrazine (see above).

Triazole Carboxylic Acids: **Triazole-3-carboxylic Acid**, $C_2H_2(COOH)N_3$, melts with decomposition at 137°. It is produced in the oxidation of methyl triazole and when $KMnO_4$ acts upon n-amidophenyltriazole carboxylic acid. **n-Phenyl triazole-3-carboxylic Acid**, $C_2H(COOH)N_3 . C_6H_5$, melting at 184°, is derived from phenylmethyl triazole as well as by the exit of CO_2 from **n-phenyltriazole-3,5-dicarboxylic acid**, $C_2(CH_3)(COOH)N_3 . C_6H_5$, which is prepared by the oxidation of **n-phenyl-5-methyl triazole-3-carboxylic acid**, $C_3(CH_3)(COOH)N_3 . C_6H_5$, melting at 177°. The latter results from the saponification of its nitrile, as well as by the moderated oxidation of acetylphenylmethyl triazole.

Bistriazoles are formed in the action of acids (and their anhydrides) upon cyanhydrazine and -phenylhydrazine (B. **26**, 2389) (B. **21**, 3063; **30**, 1194):



Cyanphenylhydrazine Bis-phenylmethyl Triazole.

Bistriazole, $(C_2H_2N_3)_2$, from cyanhydrazine and formic acid, is a compound subliming above 300°.

Hydrotriazole Derivatives: The **triazolons** are keto-derivatives of dihydrotriazoles. They can also be viewed as oxytriazoles (compare pyrazolons, p. 486, and C. 1897, II, 269). They are produced (1) by the interaction of acetyl methane and phenylhydrazines (Andreocci, B. **22**, R. 737):

$$\begin{matrix} CH_3—CO \\ NH—COOR \end{matrix} + NH_2 . NHC_6H_5 \longrightarrow \begin{matrix} CH_3—C = N \\ HN — CO \end{matrix}\!\!>NHC_6H_5.$$

The reaction suggests the formation of phenylmethylpyrazolon from acetoacetic ester and phenylhydrazine. Acetyl urethane is acetoacetic ester in which the CH_2-group has been replaced by NH (see above).

1-Phenyl-5-triazolon, $C_6H_5N — N = CH — NH — CO$, melting at 183°, has been prepared from its carboxylic acid—**1-phenyl-5-triazolon-3-carboxylic acid**. The latter is produced when $KMnO_4$ acts upon **1-phenyl-3-methyl-5-triazolon**, melting at 167° and boiling above 300° (B. **24**, R. 203).

With these 1,5-triazolons, isomeric 1,3-triazolons or oxytriazoles are produced (1) on digesting acid derivatives of phenylsemicarbazide with dilute alkali (B. **29**, 1946):

$$C_6H_5N<\begin{matrix} COR \\ NH—CO . NH_2 \end{matrix} \longrightarrow C_6H_5N<\begin{matrix} CR = N \\ NH—CO \end{matrix}.$$

(2) By the condensation of phenylsemicarbazide with aromatic aldehydes in the presence of an oxidant (C. 1897, I, 809), which probably first changes the phenylsemicarbazide to phenylazocarbamide:

$$C_6H_5NH.NH.CONH_2 \longrightarrow C_6H_5N : N.CONH_2 + OCH.CH_3 \longrightarrow \begin{matrix} C_6H_5N—NHCO \\ C_6H_5C \!=\!=\!=\! N \end{matrix}.$$

1-Phenyl-3-triazolon, $C_6H_5N . NH . CO . N : CH$ or $C_6H_5N . N : C(OH)N : CH$, from phenylsemicarbazide and formic acid, sublimes and melts at very high temperatures. **1-Phenyl-5-ethyl-, -propyl-, -isobutyl-3-triazolon** melt at 192°, 160°, and 165°.

1,5-Diphenyl-3-triazolon, melting at 290°, is obtained from benzoylphenylsemicarbazide as well as from phenylsemicarbazide and benzaldehyde. **1-Phenyl-5-styrenyl-3-triazolon**, $C_2HN_3O(C_6H_5)(CH : CHC_6H_5)$, melting at 287°, is formed from cinnamylphenylsemicarbazide, or cinnamic aldehyde and phenylsemicarbazide.

The triazolons are converted into triazoles by distillation with P_2S_5, or, better, by conversion into chlortriazoles and the reduction of the latter (B. **29**, 2671).

The **urazoles** are the diketo-derivatives of tetrahydrotriazole. They result on heating urea and its derivatives—*e.g.*, allophanic ester, biuret, etc.—with hydrazine salts:

$$\begin{array}{l} CO-NH_2 \\ | \\ NH-CO-NH_2 \\ \text{Biuret} \end{array} \xrightarrow{NH_2.NH_2} \begin{array}{l} CO-NH \\ | \\ NH-CO \\ \text{Urazole.} \end{array} \!\!>\!NH(+ 2NH_3)$$

Urazole, 3,5-*Diketotriazolidine*, $C_2H_3O_2N_3$, melting at 244°, is obtained from hydrazodicarbonamide, $NH_2 . CO . NH . NH . CO . NH_2$ (A. 283, 16). Urazole is a strong monobasic acid. It yields triazole when distilled with P_2S_5. **1-Phenyl Urazole,** $C_6H_5N - NH - CO - NH - CO$, melting at 263°, is formed from urea and phenylhydrazine, from phenylsemicarbazido-carboxylic ester (B. 28, 829), as well as from phenylhydrazido-oxalhydroxamic acid, $H_2N - \underset{\underset{NOH}{\|}}{C} - CONHNHC_6H_5$, by Beckmann's transposition (A. 295, 136). Methyl iodide converts it into *dimethylphenylurazole*, melting at 90°. Isomeric **3-Phenylurazole,** $C_6H_5N - CO - NH - NH - CO$, melting at 203°, is formed by the interaction of hydrazo-dicarbonamide and aniline hydrochloride (*l. c.*).

Thio- and *imido*-derivatives of urazole have been obtained from the corresponding thiourea- and guanidine-compounds of hydrazine (B. 29, 2506):

Thiourazole, $NH . CS . NH . CO . NH$, melting at 177°, is obtained from hydrazo-thio-dicarbonamide, $NH_2CS.NH.NH.CONH_2$. **Dithiourazole,** $NH . CS . NH . CS . NH$, melting at 245° with decomposition, and **imido-thiourazole,** $NH . CS . NH . C(NH).NH$, melting at 222°, are formed simultaneously when strong hydrochloric acid acts upon hydrazodithiodicarbonamide (B. 29, 2506).

Diimidourazole, Guanazole, $NH . C(NH) . NH . C(NH) . NH$, melting at 206°, is obtained from hydrazine and dicyandiamide by the action of hydrazine (B. 27, R. 583):

$$\begin{array}{l} C : N\diagup NH_2 \\ | \\ NH-C{=}NH \\ \text{Dicyandiamide} \end{array} + NH_2NH_2 \longrightarrow \begin{array}{l} HN : C-NH \\ | \\ HN-C{=}NH \\ \text{Guanazole.} \end{array}\!\!>\!NH$$

14. FURAZANES OR FURO[aa₁]DIAZOLES.

The furazanes or *azoxazoles*, *furo*-[aa₁]-*diazoles*, $\begin{array}{l} CH = N\diagdown \\ | \\ CH = N\diagup \end{array}\!O$ (1, 483), correspond to the osotriazoles. Just as the latter are obtained from the osazones (p. 508), so furazanes are produced from the glyoximes, the dioximes of o-diketones, or their oxidation products, the glyoxime-peroxides (B. 28, 69), by the action of alkalies:

$$\begin{array}{l} C_6H_5 . C = NOH \\ | \\ C_6H_5 . C = NOH \\ \text{Benzil Dioxime} \end{array} \longrightarrow \begin{array}{l} C_6H_5C = NO \\ | \qquad\quad | \\ C_6H_5C = NO \\ \text{Diphenylglyoxime Peroxide} \end{array} \longrightarrow \begin{array}{l} C_6H_5-C = N\diagdown \\ | \\ C_6H_5-C = N\diagup \\ \text{Diphenylfurazane.} \end{array}\!O$$

As we observed in connection with the isoxazoles, those furazane derivatives in which the H-atoms of both methine groups are substituted are stable bodies. If one of the groups is free, a rearrangement into nitriles of *a*-ketonic acid oximes may readily take place. The alkyl furazanes can be oxidized to furazane carboxylic acids.

Phenyl Furazane, $C_2H(C_6H_5)N_2O$, melting at 30°, is very volatile. It is formed when soda acts upon phenylglyoxime diacetate. Sodium hydroxide converts it readily into the oxime of benzoyl cyanide, $\begin{array}{l} C_6H_5C = N\diagdown \\ | \\ HC = N\diagup \end{array}\!O \rightarrow \begin{array}{l} C_6H_5C = NOH \\ | \\ CN \end{array}$ (B. 24, 3503).

It is stable toward acids. **Dimethyl Furazane,** $C_2(CH_3)_2N_2O$, melting at —7° and boiling at 156°, results when dimethyl glyoxime is heated with ammonia to 160–170°. **Methyl Ethyl Furazane,** $C_2(CH_3)(C_2H_5)N_2O$, boiling at 170°, is similarly obtained from methyl ethyl glyoxime. **Diphenyl Furazane,** $C_2(C_6H_5)_2N_2O$, melting at 94° (p. 373), rearranges itself by prolonged heating into isomeric *dibenzenylazoxime* (see below) (A. **264**, 180). **Dibenzoyl Furazane,** $C_2(COC_6H_5)_2N_2O$, melting at 118°, is prepared from dibenzoylglyoxime peroxide (B. **26**, 529) (p. 381).

Furazane Carboxylic Acid, $C_2H(COOH)N_2O$, melting at 107°, on oxidation becomes **furazane propionic acid,** the anhydride of dioximidovaleric acid (1, 483). **Methyl Furazane Carboxylic Acid,** $C_2(CH_3)(COOH)N_2O(+H_2O)$, melting at 74° (39°), and **Furazane Dicarboxylic Acid,** $C_2(COOH)N_2O$, melting at 178° with decomposition, are formed when potassium permanganate acts upon dimethylfurazane. The dicarboxylic, like the monocarboxylic acid, is easily converted by boiling water into cyanimidoacetic acid.

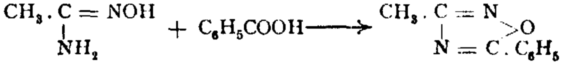
Consult B. **28**, 723, vol. 1, 500, for **oxyfurazane carboxylic acid.**

Benzo-, naphtho-, phenanthro-furazanes, etc., have been prepared from the o-dioximes of the benzene, naphthalene, and phenanthrene series (see also B. **29**, R. 790).

15. AZOXIMES OR FURO[ab₁]DIAZOLES.

The azoximes, *furo*[a,b₁]*diazoles*, $\begin{matrix} CH = N \\ | \\ N - CH \end{matrix}\!>\!O$, correspond to the triazoles or pyrro-[ab₁]diazoles, and just as they are obtained from the amidrazones (p. 511), so the azoximes are prepared:

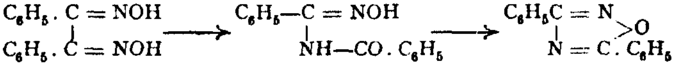
1. From amidoximes and carboxylic acids (their chlorides or anhydrides):



Ethenyl Amidoxime — Ethenylbenzenyl Amidoxime.

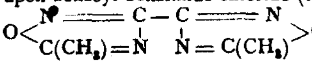
The amidoximes combine with the aldehydes of the fatty series to form *hydrazoximes*, which part readily with hydrogen and become azoximes. $COCl_2$ and $CSCl_2$ form *carbonylazoximes* (furo[ab₁]diazolons) and *azoximthiocarbinols* (B. **19**, 1487; **22**, 2422; **28**, 2231).

2. Azoximes are also prepared by Beckmann's transposition from glyoximes or furazanes (p. 381) (B. **27**, R. 800):



Benzil Dioxime — Dibenzenyl Azoxime.

Diethenyl Azoxime, $C_2(CH_3)_2N_2O$ (B. **17**, 2755), is a very volatile body. **Ethenyl Benzenyl Azoxime,** $C_2(CH_3)(C_6H_5)N_2O$, melts at 41°. **Dibenzenyl Azoxime,** $C_2(C_6H_5)_2N_2O$, melting at 108° and boiling at 290°, also results when hydroxylamine acts upon benzoyl benzimide chloride (A. **296**, 284). **Oxalenbisazoximethenyl,**



melts at 165° (B. **22**, 2949).

Benzenyl Carbonyl Azoxime, $\begin{matrix} C_6H_5C = N \\ NH - CO \end{matrix}\!>\!O$, melting at 198°, and **Benzenylazoxim-thiocarbinol,** $\begin{matrix} C_6H_4C = N \\ | \\ N = C(SH) \end{matrix}\!>\!O$, melting at 131°, are produced from benzenylamidoxime by means of $COCl_2$ and $CSCl_2$.

16. OXYBIAZOLES OR FURO[bb₁]DIAZOLES.

Hypothetical oxybiazole, or *furo*[b,b$_1$]*diazole*, $\begin{array}{l} N = CH \\ | \\ N = CH \end{array} \!\!> O$, yields—

Diphenyloxybiazole, *Dibenzenyl Isazoxime*, $N_2C_2(C_6H_5)_2O$, melting at 140°, which is isomeric with dibenzenylazoxime and diphenyl furazane. It is prepared, like them, from benzil dioxime (A. **252**, 60):

$$\begin{array}{l} C_6H_5C = NOH \\ | \\ C_6H_5C = NOH \end{array} \xrightarrow{PCl_5} \begin{array}{l} N = C(C_6H_5)Cl \\ | \\ N = C(C_6H_5)Cl \end{array} \xrightarrow{NO_3Ag} \begin{array}{l} N = C(C_6H_5) \\ | \\ N = C(C_6H_5) \end{array} \!\!> O$$

α-Benzil Dioxime — Diphenyloxybiazole.

Furthermore, it also results when nitrous acid acts upon dibenzenylhydrazidine (p. 205) (B. **27**, 984):

$$\begin{array}{l} N = C(C_6H_5)NH_2 \\ | \\ N = C(C_6H_5)NH_2 \end{array} \xrightarrow{N_2O_3} \begin{array}{l} N = C(C_6H_5) \\ | \\ N = C(C_6H_5) \end{array} \!\!> O (+ 2N_2 + 2H_2O).$$

Ditolyloxybiazole, $N_2C_2(C_7H_7)_2O$, melting at 234°, is formed from ditolenylhydrazidine (B. **27**, 3288).

The **Keto-, thio-, or imido-oxybiazolines** are derivatives of *dihydro-oxybiazole* or *oxybiazoline*. They are produced from carboxylic and urea derivatives of phenylhydrazine, naphthyl hydrazine, etc. (pp. 126, 127), through the action of phosgene, $COCl_2$, thiophosgene, $CSCl_2$, and phenyl isocyanogen chloride, $CCl_2 : NC_6H_5$ (B. **23**, 2843; **24**, 4178; **26**, 2870):

$$(1)\ \begin{array}{l} C_6H_5 . NH \\ | \\ NH . CO . CH_3 \end{array} + COCl_2 \longrightarrow \begin{array}{l} C_6H_5N - CO \\ | \\ N = C(CH_3) \end{array} \!\!> O$$

Acetyl Phenylhydrazine — n-Phenyl Methyl Oxybiazolon, m. p. 280°

$$(2)\ \begin{array}{l} C_{10}H_7NH \\ | \\ NH . CO . NH_2 \end{array} + CSCl_2 \longrightarrow \begin{array}{l} C_{10}H_7N - CS \\ | \\ N = C(NH_2) \end{array} \!\!> O$$

Naphthyl Semicarbazide — n-Naphthylamidothio-oxybiazoline, m. p. 218°

$$(3)\ \begin{array}{l} C_6H_5 . NH \\ | \\ NH . CHO \end{array} + CCl_2 : N . C_6H_5 \longrightarrow \begin{array}{l} C_6H_5N - C : (NC_6H_5) \\ | \\ N = CH \end{array} \!\!> O$$

Formylphenylhydrazine — n-Phenyl-phenylimido-oxybiazolon, m. p. 99°.

17. The ring of *furo*[ab]*diazole*, $\begin{array}{l} CH - O \\ \| \\ CH - N \end{array} \!\!> N$, is only found condensed with benzene or naphthalene nuclei in **diazo-oxides**:

Dichlor-o-diazophenol, $C_6H_2Cl_2 \!<\! \begin{array}{l} O \\ N \end{array} \!\!> N$, is formed by the action of N_2O_3 upon dichlor-o-amidophenol. **Nitro-o-diazophenol,** $C_6H_3(NO_2) \!<\! \begin{array}{l} O \\ N \end{array} \!\!> N$, from p-nitro-o-amidophenol, deflagrates at 100° (B. **2**, 52; A. **113**, 212).

Naphthalene-2,1-diazo-oxide, $C_{10}H_6 \left\{ \begin{array}{l} [2]N \\ [1]O \end{array} \right. \!\!> N$, melting at 76°, results upon oxidizing an alkaline naphthalene solution with potassium ferricyanide solution. **6-Nitronaphthalene-2,1-diazo-oxide,** $C_{10}H_5(NO_2)(N_2O)$, from 6,2-dinitro-1-diazo-naphthalene, is a substance exploding at 145° (B. **27**, 680, 2214).

The thiodiazole ring derivatives, corresponding to azoximes, oxybiazoles, and diazo-oxides, which contain furodiazole rings, occur in the groups of the *azosulphimes, thio-*

biazoles, and *diazosulphides*. *Piazthiolen* is a thiodiazole ring analogous to the furazane ring.

18. **Azosulphimes, or Thio[ab$_1$]diazoles**: $\begin{matrix} CH = N \\ | \\ N = CH \end{matrix} \!\!>\! S$, result from the action of carbon disulphide upon amidoximes (B. **24**, 388):

$$\begin{matrix} C_6H_5C = N.OH \\ | \\ NH_2 \end{matrix} + CS_2 \longrightarrow \begin{matrix} C_6H_5C = N - \\ | \\ N = C(SH) \end{matrix} \!\!>\! S$$

Benzenyl Amidoxime — Benzenylazosulphime Sulphydrate, m. p. 162°.

Azosulphime anilides are formed when phenyl mustard oil is used.

Dibenzenyl Azosulphime, $\begin{matrix} C_6H_5C = N - \\ | \\ N = C(C_6H_5) \end{matrix} \!\!>\! S$, results from the action of iodine upon thiobenzamide (B. **25**, 1586).

19. The **thiobiazolines** are derivatives of *thio*[bb$_1$]*diazole*, $\begin{matrix} N = CH \\ | \\ N = CH \end{matrix} \!\!>\! S$. They result from the action of aldehydes upon phenylsulphocarbazinic acid (p. 126), or, better, their ethers (B. **28**, 2635):

$$\begin{matrix} C_6H_5.NH \\ | \\ HN - CSSH \end{matrix} + CH_2O \longrightarrow \begin{matrix} C_6H_5N - CH_2 - \\ | \\ N = C(SH) \end{matrix} \!\!>\! S$$

Phenylsulphocarbazinic Acid — 2-Phenylthiobiazoline Sulphydrate, m. p. 112°.

The thiobiazoline sulphydrates formed in this manner are very acid. They are stable toward acids. Aqueous alkalies decompose them. They oxidize quite easily to *disulphides*. See l. c. for the rearrangement of the latter (B. **29**, 2127).

Amido-derivatives of the thiobiazolines are prepared from the thiosemicarbazides with aldehydes (B. **30**, 849):

$$\begin{matrix} C_6H_5NH \quad\; \\ | \qquad\quad\;\; \diagup SH \\ N = C(NHC_6H_5) \end{matrix} + OCH.C_6H_5 \longrightarrow \begin{matrix} C_6H_5N - CH(C_6H_5) \\ | \\ N = C(NHC_6H_5) \end{matrix} \!\!>\! S$$

Diphenylthiosemicarbazide — Anilidophenylthiobiazoline, m. p. 106°.

(1) *Imidothiobiazolines*, (2) *ketothiobiazolines* or *pseudothiobiazolons*, and (3) *dithiobiazolines* are made by the action of carboxylic acids, $COCl_2$ and CS_2, upon thiourea- and dithio-carbamic acid derivatives of the hydrazines (p. 126; **24**, 4190; **27**, 613, 2512; **29**, 2483):

$$(1)\ \begin{matrix} NH_2 \\ | \\ NH - CSNHC_6H_5 \end{matrix} + HCOOH \longrightarrow \begin{matrix} N = CH - \\ | \\ NH - C(:NC_6H_5) \end{matrix} \!\!>\! S$$

Phenylthiosemicarbazide — c-Phenylimidothiobiazoline, m. p. 173°.

Imidothiobiazoline, S.C(NH).NH.N:CH, melting at 191°, is obtained from formylthiosemicarbazide (B. **29**, 2511). It is remarkable that the acidylthiosemicarbazides, when deprived of water by acetyl chloride, yield thiobiazolines, but when heated above their melting point, mercaptotriazoles result:

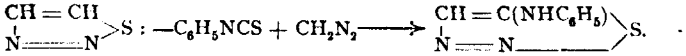
$$(2)\ \begin{matrix} C_{10}H_7NH \\ | \\ NH - CS.NH_2 \end{matrix} + COCl_2 \longrightarrow \begin{matrix} C_{10}H_7N - CO - \\ | \\ N = C(NH_2) \end{matrix} \!\!>\! S$$

Naphthylsulphosemicarbazide — n-Naphthylamido-ψ-thiobiazolon, m. p. 250°.

$$(3)\ \begin{matrix} C_6H_5N \\ | \\ NH - CSSH \end{matrix} + CS_2 \longrightarrow \begin{matrix} C_6H_5N - CS - \\ | \\ N = C(SH) \end{matrix} \!\!>\! S$$

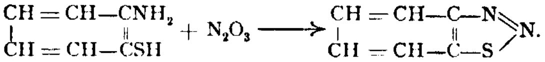
n-Phenyldithiobiazoline Sulphydrate, m. p. 91°.

20. **The addition product of phenyl mustard oil with diazomethane may be viewed as a derivative of Thio[ab]diazole:**



α-Anilidothio[ab]diazole melts at 172° with decomposition. The *acetyl derivative* melts at 162°; the *nitroso*-derivative melts at 98° (B. 29, 2588).

The **phenylene diazosulphides** are *benzo*-derivatives of thio[ab]diazole. They correspond to the diazo-oxides and azoïmides. They are produced when nitrous acid acts upon o-amidothiophenols:

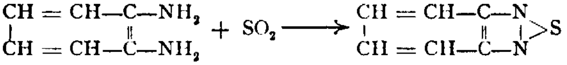


o-Amidothiophenol — Phenylene Diazosulphide.

The diazosulphides are more stable than the diazo-oxides. They resemble the azoïmides more particularly, as they only give up their nitrogen at higher temperatures, and then without deflagration. In doing this they yield diphenylene disulphides: $C_6H_4<{S \atop S}>C_6H_4$. The diazosulphides are feeble bases and take up alkyl iodides (A. 277, 214).

Phenylene Diazosulphide, $C_6H_4N_2S$, melts at 35° and boils at 129° (10 mm.).
Cumylene Diazosulphide, $C_6H(CH_3)_3N_2S$, melts at 85°.

21. The ring of *thio*[aa$_1$]*diazole*, ${C-N \atop C-N}>S$, unites with the benzene nucleus to form **Piazthioles,** which also result upon treating the o-phenylenediamines with sulphurous acid (B. 22, 2895):



o-Phenylene Diamine — Piazthiole, m. p. 44°, b. p. 206°.

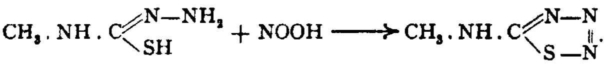
The piazthioles are feebly basic bodies, which are very stable toward oxidants. The o-diamines result from their reduction.

The **piaselenoles** correspond to the piazthioles. They are similarly formed from o-diamines and selenious acid. In their stability they resemble the piazthioles.

Piaselenol, $C_6H_4<{N \atop N}>Se$, melts at 76°.

Tolupiaselenol, $C_7H_6(N_2Se)$, melts at 73° and boils at 267°.

22. **Thio[abb$_1$]triazoles, or Triazsulpholes,** ${CH = N \atop N = N}>S$: A series of compounds may be referred to this ring. They result from the action of nitrous acid upon thiosemicarbazide and alkylic thiosemicarbazides, whereas phenylthiosemicarbazide yields a tetrazole compound (B. 29, 2491):



The amidotriazsulpholes formed in this manner decompose, when boiled with water, into sulphur, nitrogen, and cyanamides, while with concentrated hydrochloric acid they yield nitrogen and *thiocyanamides*:

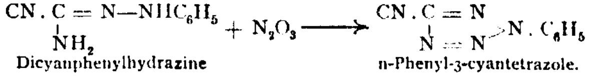
Methylamido-, ethylamido-, and allylamido-triazsulpholes melt at 96°, 67°, and 54°. Amido-triazsulphole, from thiosemicarbazide and N_2O_3, deflagrates at 128–130°.

23. TETRAZOLES.

Two isomeric series of tetrazoles are possible. They can be distinguished as *Pyrro*-[aa_1b]*triazoles*, $\begin{matrix} CH = N \\ | \\ N - N \end{matrix}\!\!>NH$, and *pyrro*[$abb_1$]*triazoles*, $\begin{matrix} N = CH \\ | \\ N = N \end{matrix}\!\!>NH$. The syntheses do not invariably afford a certain basis for the judgment of the constitution of the tetrazoles (B. **29**, 1846).

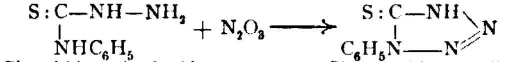
Tetrazoles are produced:

1. By the action of nitrous acid upon hydrazidines (amidrazones) (p. 205)—*e. g.*, benzenylhydrazine (B. **27**, 995), dicyanphenylhydrazine (Bladin, B. **19**, 2598), amidoguanidine (A. **273**, 144). This is similar to the formation of triazoles from the same compounds with carboxylic acids:



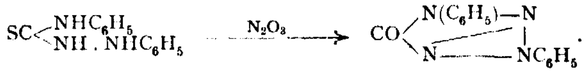
Dicyanphenylhydrazine — n-Phenyl-3-cyantetrazole.

A tetrazole derivative which might be derived from pyrro[abb_1]triazole is produced in the action of N_2O_3 upon phenylthiosemicarbazide (B. **28**, 74):



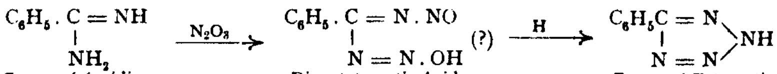
Phenylthiosemicarbazide — n-Phenyl-5-thiotetrazoline.

However, when nitrous acid acts upon diphenylthiosemicarbazide, sulphur is split off, and **Diphenylisotetrazolon** is produced:



It consists of red needles, melting at 110°. It is basic. Reduction causes it to break down again into diphenylsemicarbazide, and recalls the pseudo-azimides (p. 509) (B. **29**, 1689).

2. With nitrous acid the amidines yield dioxytetrazotic acids. These, on reduction, become oxytetrazotic and tetrazotic acids. The latter are identical with the tetrazoles which are formed by the first method (A. **263**, 101; B. **27**, 994):



Benzenyl Amidine — Dioxytetrazotic Acid — Benzenyl Tetrazotic Acid, c-Phenyl Tetrazole.

3. Finally, the tetrazoles are prepared by oxidizing suitable tetrazolium compounds, the oxidation products of formazyl derivatives (see below and p. 131).

Behavior: The tetrazole ring, composed of four N-atoms and one C-atom, shows in general equal stability with azole and pyrrol, containing less nitrogen. Thus, the n-phenylated derivatives, just as with the pyrazoles and the triazoles, can be converted by nitration into nitrophenyltetrazoles, and the amido-bodies from these may be oxidized to tetrazoles. The feebly basic character of pyrrol becomes in tetrazole a strong acid, due to the influence of the N-atoms. After comparing pyrrol in many respects with phenol, tetrazole may be arranged side by side with trinitrophenol. The *silver* and *copper* salts deflagrate violently on heating.

Tetrazole, $\begin{matrix} CH = N \\ | \\ N = N \end{matrix}\!\!>NH$, melting at 156°, sublimes and is prepared by treating diazotetrazole (see below) with alcohol (A. **287**, 243); by oxidizing amidophenyltetrazole carboxylic acid (B. **25**, 1412), as well as in the action of $KMnO_4$ upon di-p-oxydiphenyl-

tetrazolium betaïne (below). *Sodium salt*, $CN_4HNa + H_2O$; *barium salt*, $(CN_4H)_2Ba + 3\frac{1}{2}H_2O$. Tetrazole is decomposed into CO_2, N_2, and $2NH_3$ when it is heated with concentrated hydrochloric acid.

c-**Phenyl Tetrazole**, *Benzenyl Tetrazotic Acid*, $C(C_6H_5)N_4H$, melts with decomposition at 219° (A. **263**, 107). It is obtained from dioxytetrazotic acid or from benzenyl hydrazidine. c-**Tolyl**- and c-**Furyl Tetrazoles**, melting with decomposition at 234° and 199° respectively, are similarly formed from tolyl- and furylhydrazine (B. **28**, 465). n-**Phenyl Tetrazole**, $CHN_4 . C_6H_5$, from its acid, is an oil, deflagrating when heated.

Diphenyl Tetrazole, $CN_4(C_6H_5)_2$, melting at 107°, results when p-oxyphenyl-diphenyltetrazolium hydroxide is acted upon with potassium permanganate, as well as in the oxidation of guanazyl benzene, $C_6H_5C\begin{matrix}\diagup N . NH(CN_2H_3) \\ \diagdown N : N(C_6H_5)\end{matrix}$, with N_2O_3 or nitric acid. It is characterized by its great stability (B. **29**, 1854).

Bistetrazole, $(CHN_4)_2$ (?), is formed when N_2O_3 acts upon the addition product of cyanogen and hydrazine (B. **26**, R. 891).

c-**Amidotetrazole**, *Amidotetrazotic Acid*, $C(NH_2)N_4H$, melting at 203°, results when nitrous acid acts upon diazoguanidine nitrate, and by further action of the acid yields **diazotetrazole**, which explodes in concentrated aqueous solution, even at 0°. It probably has the following constitution: $C\begin{matrix}\diagup N = N \\ =N - N. \\ \diagdown N = N\end{matrix}$ Metallic oxides form stable salts with it. Their formula is $C(N : N . OMe)N_4Me$.

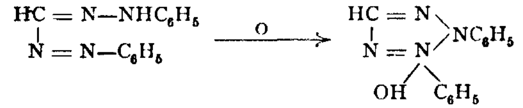
Tetrazyl Hydrazine, $C(NHNH_2)N_4H$, is produced by the reduction of diazotetrazole. It melts with decomposition at 199°. Nitrous acid converts it into **tetrazylazoïmide**, $C(N_3)N_4H$, a beautiful crystalline, exceedingly explosive substance (A. **287**, 238).

n-**Phenyl Tetrazole Carboxylic Acid**, $C(COOH)N_4C_6H_5$, melting at 138°, results upon saponifying synthetic n-**phenylcyantetrazole** (see above).

Derivatives of pyrro-[abb₁]*-triazole*:

1-**Phenyl-5-thiotetrazoline**, $S : C - NH - N = N - N . C_6H_5$ (?), melting with decomposition at 142–145°, is formed from phenylthiosemicarbazide when acted upon with nitrous acid. Digestion with caustic soda converts it into isomeric **phenyltetrazole mercaptan**, $HS . C = N - N = N - N . C_6H_5$, melting at 150°. Both compounds yield the same silver salt, which methyl iodide converts into n-*phenyltetrazolemethyl sulphide*. Potassium permanganate produces n-phenyltetrazole sulphonic acid, $C(SO_3H)N_4C_6H_5$, which, upon heating with hydrochloric acid, splits off the sulpho-group and becomes 1-*phenyl-5-oxytetrazole*, $OH . C = N - N = N - NC_6H_5$, melting at 186°.

Tetrazolium compounds are those which result from the oxidation of formazyl bodies in a manner similar to that by which the azoammonium derivatives are obtained from the o-anilido-bodies (B. **27**, 2920), and the osotetrazones from the osazones (p. 508).

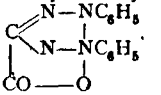


Formazyl Hydride n-Diphenyltetrazolium Hydroxide.

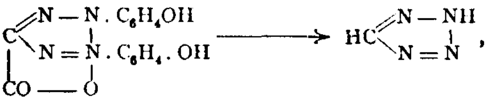
The oxidation is best effected by amyl nitrite and hydrochloric acid. The tetrazolium hydroxides are, like all ammonium hydroxides, strong bases. Ammonium sulphide reduces them to formazyl compounds.

n-**Diphenyl Tetrazolium Chloride**, $CHN_4(C_6H_5)_2Cl$, melting with decomposition at 268°, results by the elimination of carbon dioxide from **diphenyltetrazolium**

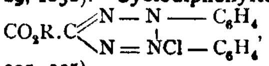
chloride carboxylic acid, melting at 257° with decomposition. The ester of this acid is prepared from formazyl carboxylic ester (p. 129), and passes just as readily as the acid into a betaine,



p_2-Dioxydiphenyl-tetrazolium Betaïne, formed in an analogous manner, melts at 179° with decomposition, and can be oxidized to tetrazole (B. 28, 1693):



which demonstrates the connection between the tetrazoles and tetrazolium compounds. Similarly, **p-monoxyphenyldiphenyltetrazolium chloride** yields diphenyltetrazole (B. 29, 1852). **Cyclodiphenyltetrazolium chloride carboxylic ester**,



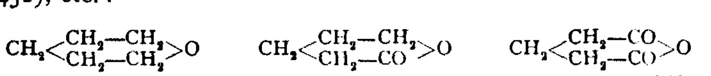
is derived from cycloformazyl carboxylic ester (p. 339; A. 295, 335).

4. SIX-MEMBERED HETEROCYCLIC COMPOUNDS.

A. MONOHETEROATOMIC SIX-MEMBERED RINGS.

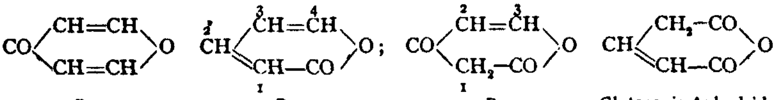
1. SIX-MEMBERED RINGS WITH AN O-MEMBER.

A series of cyclic bodies belongs here. They have already been discussed, according to their character, either with the fatty bodies or fatty aromatic substances with open chain, with which they are genetically related. They are the *anhydrides of ε-glycols* (1, 300), the *δ-lactones*,—*e. g.*, *δ-valerolactone* (1, 345),—the *anhydrides of the glutaric acids* (1, 452), etc.:



Pentylene Oxide — δ-Valerolactone — n-Glutaric Anhydride.

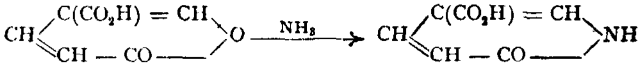
These are unsaturated δ-lactones and acid anhydrides corresponding to the saturated δ-lactones and δ-acid anhydrides. Anhydrides of unsaturated ε-glycols are not known, but there are anhydrides of diolefine dioxyketones. They are the γ-**pyrones**, which are isomeric with the diolefine-δ-oxy-acid lactones, the α-**pyrones**:



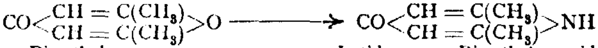
γ-Pyrone — α-Pyrone — α,γ-Pyronon — Glutaconic Anhydride.

The pyrones and allied compounds are characterized by the fact that

when they are digested with ammonia the linking oxygen atom is replaced by NH, and *pyridones* or *oxypyridines* (p. 534) result:



α-Pyrone Carboxylic Acid, Coumalic Acid — Oxypicolinic Acid



Dimethyl-γ-pyrone — Lutidone, α,α_1-Dimethyl-γ-pyridone.

a. The *coumalins* belong to the α-pyrones:

α-Pyrone, **Coumalin**, $C_5H_4O_2$, and **2,4-Dimethyl-α-pyrone, dimethyl coumalin**, $C_5H_2(CH_3)_2O_2$ (1, 362), *are obtained from their acids:*

Coumalic Acid, $C_5H_3O_2 . CO_2H$, made by the action of concentrated sulphuric acid upon malic acid, and

Dimethyl Coumalic Acid, *isodehydracetic acid*, $C_5H(CH_3)_2O_2 . COOH$, which is produced by the action of sulphuric acid upon acetoacetic ester (1, 496).

Phenyl Coumalin, 1-Phenyl-α-pyrone, $C_5H_3(C_6H_5)O_2$, melting at 68°, occurs in the coto bark. δ-Phenylvaleric acid results from its reduction. It yields α-phenylpyridine with ammonium acetate (B. **29**, 1673, 2659).

α,γ-Pyronon yields: **Dehydracetic Acid**, or **1-Aceto-3-methyl pyronon**, $C_5H_2(CH_3)(COCH_3)O_2$ (1, 521), resulting upon boiling acetoacetic ester, and

Dehydracetcarboxylic Acid, 1-Aceto-3-methylpyronon-2-carboxylic Acid, which is formed by the interaction of acetone dicarboxylic acid and acetic anhydride (1, 501, 521).

b. *γ-Pyrones* are uniformly produced by splitting off water from 1,3,5-triketones (B. **24**, 111):

Acetone Dioxalic Ester — Chelidonic Ester (see below).

Conversely, they are readily reconverted into triketones. Although the pyrones contain a ketone oxygen atom, they do not react with hydroxylamine, etc.; compare the *xanthones*, p. 524.

γ-**Pyrone, Pyrocomane**, $C_5H_4O_2$, is formed when comanic and chelidonic acids are heated. Carbon dioxide is eliminated. It melts at 32.5° and boils at 315°.

α,α_1-**Dimethyl Pyrone**, $C_5H_2O_2(CH_3)_2$, results upon heating dehydracetic acid with hydriodic acid, or when carbon dioxide is expelled from its acid (A. **257**, 253). It melts at 132° and boils at 248°. It sublimes at 80°. Boiling baryta-water converts it, with rupture of the ring, into diacetylacetone (compare dimethyl furfurane), which ammonia changes to lutidone.

Oxypyrone, $C_5H_3O_2(OH)$, *pyrocomenic acid, pyromeconic acid*, is obtained from comenic and meconic acids by distillation. It melts at 121° and boils at 228°. It forms unstable salts with bases.

Pyrone Carboxylic Acid, **Comanic Acid**, $C_5H_3O_2 . CO_2H$, is obtained from chelidonic acid by the loss of carbon dioxide. It dissolves with difficulty in water. It melts at 250° and decomposes. When boiled with lime it decomposes into acetone, oxalic acid, and formic acid. It forms an oxypicolinic acid when digested with ammonia.

Pyrone Dicarboxylic Acid, Chelidonic Acid, $C_5H_2O_2(CO_2H)_2$, melts at 220°, and occurs, together with malic acid, in *Chelidonium majus* (A. **57**, 274). It can be readily obtained through the exit of water from acetone-dioxalic acid. It forms colorless salts. An excess of alkali converts it into salts of acetone-dioxalic acid or **xanthochelidonic acid**, which are yellow-colored.

The reduction of chelidonic acid gives rise to acetone-diacetic acid or **hydro-chelidonic acid**, and normal pimelic acid. Ammonia converts it into an oxy-pyridine dicarboxylic acid (p. 537).

Oxy-pyrone Carboxylic Acid, *Comenic Acid*, $C_5H_2(OH)(COOH)O_2$, from meconic acid, is converted by ammonia into dioxypicolinic or comenamic acid (p. 538), which can also be obtained from **Meconic Acid**, $C_5H(OH)(COOH)_2O_2 + 3H_2O$, which occurs in opium in union with morphine (A. **83**, 352). It readily parts with carbon dioxide. Ferric salts color its solutions dark red.

Dimethyl Pyrone Dicarboxylic Acid, $C_5(CH_3)_2(COOH)_2O_2$; its *diethyl ester*, melting at 80°, is formed by the exit of water from carbonyl diacetoacetic ester, $CO[CH(CO_2R)COCH_3]_2$ (B. **20**, 154; also B. **24**, R. 573).

Tetrahydropyrone derivatives result from the condensation of acetone dicarboxylic esters and aldehydes by means of hydrochloric acid (B. **29**, 994, 2051):

$$CO\!<\!\begin{matrix}CH_2(CO_2R)\\CH_2(CO_2R)\end{matrix} + 2OCH.CH_3 \longrightarrow CO\!<\!\begin{matrix}CH(CO_2R)-CH(C_6H_5)\\CH(CO_2R)-CH(C_6H_5)\end{matrix}\!>\!O.$$

Dimethyl- and **diphenyl-tetrahydropyrone dicarboxylic diethyl esters** melt at 102° and 115°. Similarly, **diphenyldimethyl tetrahydropyrone**, $C_5H_4O_2(CH_3)_2(C_6H_5)_2$, melting at 106° and boiling at 236° (20 mm.), is formed from diethyl ketone and two molecules of benzaldehyde in the presence of alcoholic potash (B. **29**, 1352).

The **coumarins** and **isocoumarins** are *benzo-derivatives of a-pyrone*:

$$C_6H_4\begin{cases}[1]CH = CH\\ \quad | \qquad\quad |\\ [2]O\text{——}CO\end{cases} \qquad\qquad C_6H_4\begin{cases}[1]CH = CH\\ \quad | \qquad\quad |\\ [2]CO — O\end{cases}$$

(a-) Benzopyrone, Coumarin — Iso-[a]-benzopyrone, Isocoumarin.

The latter are more easily converted by ammonia into benzopyridone or oxyisoquinoline derivatives than the pyrones into pyridones.

Coumarin and its homologues have been discussed as lactones of o oxycinnamic acids immediately after the latter (p. 280). *Isocoumarins*, the lactones of benzene carboxylic acids, with hydroxylated side-chain unsaturated in the β-position, isomeric with the o-oxycinnamic acids, are produced by the following general methods:

1. Benzal-, xylal-, and alkylidene phthalides can be rearranged into isobenzalphthalides or isocoumarins (B. **20**, 2363; **24**, 3973):

$$C_6H_4\!<\!\begin{matrix}C{=}CH.C_6H_5\\ \;>O\\ CO\end{matrix} \longrightarrow C_6H_4\!<\!\begin{matrix}CH = CC_6H_5\\ \qquad\quad |\\ CO — O\end{matrix}$$

Benzalphthalide — Isobenzalphthalide, Phenylisocoumarin.

2. When acid anhydrides or chlorides act upon o-cyanbenzyl cyanide, condensation products result which, upon treatment with acids, have one cyanogen group split off and the other saponified, with the production of isocoumarins (B. **25**, 3566; **27**, 827):

$$C_6H_4\!<\!\begin{matrix}CH_2(CN)\\CN\end{matrix} \xrightarrow{(RCO)_2O} C_6H_4\!<\!\begin{matrix}C(CN) = CR\\ \qquad\qquad |\\ CO \qquad OOCR\end{matrix} \xrightarrow{H_2O} C_6H_4\!<\!\begin{matrix}CH = CR\\ \qquad |\\ CO — O\end{matrix}$$

Benzo- and **dibenzo-γ-pyrones** are derived from γ-pyrone. Various *yellow* vegetable dyes are to be included in this group (v. Kostanecki).

Chrysin, *fisetin*, and *quercetin* are obtained from *β-phenylbenzo-γ-pyrone*, so-called *flavone* (*flavus*, "yellow"). Judging from their decomposition products, the following formulas may probably be ascribed to them:

$$(HO)_2[3,5]C_6H_2\begin{cases}[1]O—CC_6H_5\\ \qquad\quad \|\\ [2]CO—CH\end{cases} \quad (HO)_2[3,5]C_6H_2\begin{cases}[1]O—CC_6H_3(OH)_2\\ \qquad\quad \|\\ [2]O—C(OH)\end{cases} \quad HOC_6H_3\begin{cases}[1]O—CC_6H_3(OH)_2\\ \qquad\quad \|\\ [2]O—C(OH)\end{cases}$$

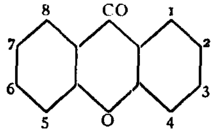
Chrysin — Quercetin — Fisetin.

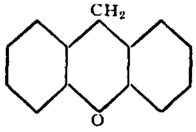
Chrysin, $C_{15}H_{10}O_4$, melting at 275°, occurring in the blossoms of different poplars, may be decomposed into phloroglucin, benzoic acid, and acetic acid.

Fisetin, $C_{15}H_{10}O_6$, from *Rhus catinus*, and *Quebracho Colorado* (B. **29**, R. 853), can be resolved into resorcinol, protocatechuic acid, and glycollic acid, while **Quercetin**, $C_{15}H_{10}H_7$, melting at 250°, and obtained from the glucoside quercitrin, found in the bark of *Quercus tinctoria*, as well as from the buds of the horse-chestnut, and from onions (B. **29**, R. 779), may be broken down into phloroglucin, protocatechuic acid, and glycollic acid (B. **28**, 2302).

Myricetin, $C_{15}H_{10}O_8$, a yellow dye present in the bark of *Myrica nagi*, is probably *oxyquercetin*, with the formula $(OH)_2[3,5]C_6H_3\left\{\begin{matrix}[1]O\text{——}CC_6H_2(OH)_3\\ \| \\ [2]CO - C(OH)\end{matrix}\right.$ (B. **29**, R. 778). Compare B. **30**, 1077, for the synthesis of flavone and its derivatives.

The **Xanthones** (ξανθός, yellow) or *diphenylene ketone oxides* are dibenzopyrones. They can also be viewed as keto-derivatives of **Xanthene**, or *methylenediphenylene oxide* (B. **26**, 72):





The xanthones possess a *chromogenic* nature. They are allied to thioxanthones (p. 526), the acridones (p. 560), and thiodiphenylamines. Generally they are formed by condensing salicylic acid with phenols through the agency of sulphuric acid, acetic anhydride, etc. (B. **21**, 502):

$$(HO)C_6H_3{<}^{H}_{OH} + {}^{OH\,.\,CO}_{OH}{>}C_6H_4 \longrightarrow (HO)C_6H_3{<}^{CO}_{O}{>}C_6H_4$$

Resorcinol — Salicylic Acid — Oxyxanthone.

Xanthene, *Methylene Diphenylene Oxide*, $C_{13}H_{10}O$, melting at 99° and boiling at 312°, is produced by the reduction of xanthone and oxyxanthones. o-Dioxybenzophenone is formed when it is fused with caustic potash (p. 348). **Tetramethyldiamidoxanthene**, *Tetramethyldiamidodiphenyl methane oxide*, $(CH_3)_2NC_6H_3{<}^{CH_2}_{O}{>}C_6H_3N(CH_3)_2$, melting at 116°, obtained by the action of sulphuric acid upon tetramethyldiamidodioxydiphenylmethane, the leuco-base of the dye pyronine (see below) (B. **27**, 3303). **Dinaphthoxanthene**, $C_{10}H_6{<}^{CH_2}_{O}{>}C_{10}H_6$, melting at 199°, results upon condensing formic aldehyde with β naphthol (p. 410) (B. **26**, 84).

Xanthydrol, $C_6H_4{<}^{CH(OH)}_{O}{>}C_6H_4$, is formed in the careful reduction of xanthone. It is a substance which changes quite readily. Like benzhydrol (p. 344), it shows a great tendency to split off water and pass into its ether—**xanthydrol ether**, $(C_{13}H_9O)_2O$, melting at 200° (B. **26**, 1276; compare also B. **28**, 2310).

Xanthone, Diphenylene Ketone Oxide, $C_{13}H_8O_2$, melting at 174° and boiling at 250°, is produced from salicylic phenyl ether or phenylsalicylic acid by the action of concentrated sulphuric acid from o_2-diamidobenzophenone with nitrous acid (B. **27**, 3363); and when fluorane and hydrofluoranic acid (p. 365) are distilled with lime (B. **25**, 2119). It does not unite with hydroxylamine or phenylhydrazine. It forms dioxy-benzophenone on careful fusion with KOH.

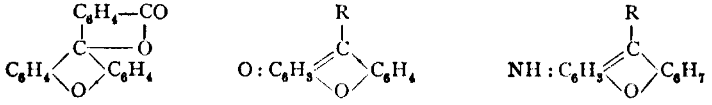
Just as benzophenone yields tetraphenylethylene, so xanthone is converted by zinc-dust, hydrochloric acid, and acetic acid into *tetraphenylene-ethylene dioxide*, $O[C_6H_4]_2 : C : C[C_6H_4]_2O$, melting at 315° (B. **28**, 2311).

Oxyxanthones, $C_{13}H_7(OH)O_2$: The four possible isomerides have been prepared by condensing salicylic acid with resorcinol, hydroquinone, and pyrocatechol (B. **25**, 1652; **26**, 71).

Euxanthone, 1,7-Dioxyxanthone, $HOC_6H_3{<}\genfrac{}{}{0pt}{}{CO}{O}{>}C_6H_3OH$, consists of yellow needles melting at 237° and subliming. It occurs free and in combination with glycuronic acid (1, 585) as euxanthinic acid in Indian yellow. It has been synthetically produced by the action of acetic anhydride upon two molecules of β-resorcylic acid and hydroquinone carboxylic acid (B. **24**, 3982; **27**, 1989; A. **254**, 265).

3,6-**Dioxyxanthone** results on heating o_2,p_2-tetraoxybenzophenone, a decomposition product of fluoresceïn chloride in the alkali fusion. It consists of colorless needles. Its alkaline solutions show a deep violet-blue fluorescence (B. **30**, 969). **1,3,7-Trioxyxanthone, Gentiseïn**, $C_{13}H_7(OH)_3O_2(+2H_2O)$, melting at 315°, is obtained synthetically from hydroquinone carboxylic acid and phloroglucin. It dyes mordanted cotton a bright yellow. **Gentisin** (B. **27**, 190; **29**, R. 221), occurring in the root of *Gentiana lutea*, is its monomethyl ether. Compare B. **25**, 1641, for the **dinaphthoxanthones, phenonaphthoxanthones**, etc.

The **fluoranes, fluorones**, and **fluorimes** are related to the xanthones (B. **25**, 2119; **27**, 2887):

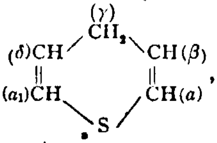


Fluorane Fluorone Fluorime.

These are the parent-substances of the fluoresceïn dyes (pp. 363, 366). **Pyronine**, $(CH_3)_2N.C_6H_3{<}\genfrac{}{}{0pt}{}{CH}{O}{>}C_6H_3N(CH_3)_2Cl$, belongs to the fluorimes. It is produced by the exit of water from and the oxidation of dioxytetramethyldiamidodiphenylmethane. The leuco-compound of pyronine is 2,7-**Tetramethyldiamidoxanthene**, melting at 116°. Pyronine may be oxidized in alkaline solution to **tetramethyldiamidoxanthone**, melting at 241°. Pyronine colors silk and imparts a beautiful rose-color to cotton (B. **27**, 2896, 3304; **29**, R. 1129).

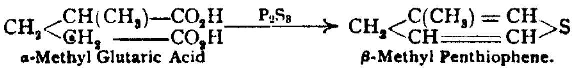
2. SIX-MEMBERED RINGS CONTAINING ONE S-MEMBER.

Six-membered rings containing sulphur as the hetero-atom are present in the derivatives of hypothetical **penthiophene**,



a ring-homologue of thiophene. They are, however, not very numerous.

β-Methyl Penthiophene, $C_5H_5(CH_3)S$, is an oil boiling at 134° with sp. gr. 0.994 (19°). It is produced from α-methyl glutaric acid by the action of P_2S_3, similar to the formation of thiophene from succinic acid (p. 453) (B. **19**, 3266):



α-Methyl Glutaric Acid β-Methyl Penthiophene.

It is colored the same as the thiophenes by isatin or penanthraquinone and sulphuric acid. It is more unstable than the thiophenes and is destroyed completely by very dilute potassium permanganate. Acetyl chloride and Al_2Cl_6 convert it into **acetyl methyl penthiophene**, $C_5H_4(COCH_3)(CH_3)S$, boiling at 250°.

A *dibenzoderivative of penthiophene* is found in **Thioxanthene** or *methylene diphenylene sulphide*, $C_6H_4<{}^{CH_2}_{S}>C_6H_4$, melting at 128° and boiling at 340°. It is obtained pyrogenically from phenyl-tolyl sulphide, and by reducing its ketone with hydriodic acid and phosphorus.

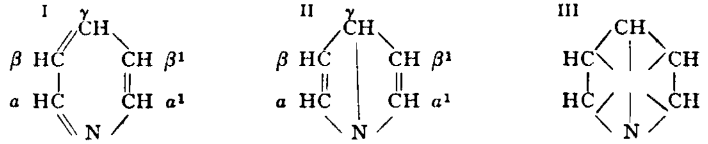
Thioxanthone, *benzophenone sulphide*, $C_{13}H_8OS = C_6H_4<{}^{CO}_{S}>C_6H_4$, melting at 207° and boiling at 340°, is the ketone of the preceding body. Being an analogue of xanthone, it is formed similarly to the latter from thiophenylsalicylic acid and sulphuric acid (A. **263**, 1). It forms a *sulphone*, $C_6H_4<{}^{CO}_{SO_2}>C_6H_4$, on oxidation.

3. SIX-MEMBERED RINGS CONTAINING AN N-MEMBER.

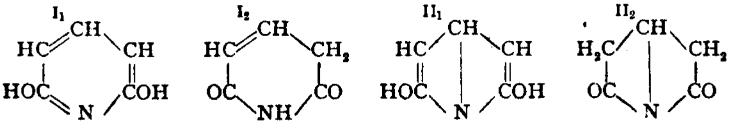
1. PYRIDINE GROUP.

Pyridine, C_5H_5N, is the parent substance of many vegetable alkaloids. Its compounds, like those of benzene, show great stability toward oxidizing agents, inasmuch as those having side-chains—*e. g.*, the alkyl pyridines, $C_5H_4(CH_3)N$, $C_5H_3(CH_3)_2N$, etc.—are converted on oxidation, like the alkyl benzenes, into acids, the pyridine nucleus not being attacked. As in the case of the aromatic derivatives, this behavior is assumed to be due to the existence of a six-membered ring, consisting of five carbon atoms and one nitrogen atom, similar to the six-membered benzene ring. Pyridine is the hydrogen derivative of this ring: it is benzene in which one CH- or methine group is replaced by a nitrogen atom.

The following structural formulas have been proposed for pyridine: (1) the formula of Körner; (2) the formula of Riedel. They differ in that in Körner's formula the nitrogen atom is linked to *two* carbon atoms, while in that of Riedel it is combined with *three* carbon atoms. To this formula that (3) of Bamberger and v. Pechmann adds itself. It is a centric formula (B. **24**, 3151), for which there are no experimental proofs (see p. 40):



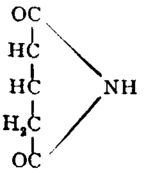
To determine whether pyridine contained an N-atom in union with two or three carbon atoms, Kekulé* arranged a series of experiments based on the following considerations. Assuming that in the pyridine formulas I and II the α-hydrogen atoms are replaced by two hydroxyl groups, the connection between the nitrogen and the carbon atom now carrying oxygen will be less intimate. This becomes evident if we imagine that the C(OH)-groups have rearranged themselves into the keto-form:



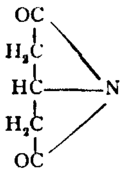
* B. **23**, 1265, and private communications.

The ordinary mode of writing pyridine obscures the connection of these pyridine derivatives with the aliphatic bodies, the derivatives of which they may be considered. This relation is more evident from the following representations:

I_2



II_2



It becomes at once plain that formula I_2 represents a glutaconic acid derivative—the imide of glutaconic acid; while formula II_2 is a β-amidoglutaconic acid derivative—an inner imide of β-amidoglutaric acid. According to formula II_2 the inner imide of β-amidoglutaric acid would have a constitution similar to that suggested by Kekulé for furarimide, and as the latter is supposed to be prepared from ammonium malate, Kekulé began with *β-oxyglutaric acid* (1, 494), and attempted by heating its ammonium salt to prepare homofumarimide, but without result. Again, he sought to pass from *β-oxyglutaric acid diamide* ($+ 2H_2O$), from *glutaconamic acid* and *glutacondiamide*, to pyridine. In fact, these three substances, when acted upon with concentrated sulphuric acid, yield *glutaconimide* or *dioxypyridine* (1, 467) of formula I_2.

The presence of the imido-group was proved by converting the sodium compound of glutaconimide into *methyl glutaconimide*, from which hydriodic acid liberates methylamine, and by the preparation of *nitrosoglutaconimide*. The decomposition of glutaconimide gave glutaconic acid. The objection that here β-amido-glutaric acid was first produced in conformity with formula II_2, and that from this glutaconic acid arose through the elimination of ammonia, is contradicted by the deportment of the β-amidoglutaric acid, which, under like conditions, does not yield glutaconic acid. The β-amidoglutaric acid, too, yielded no glutaconimide, or any amount of an isomeric body; the ring-formation failed.

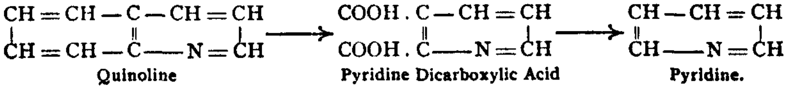
The connection of glutaconimide with pyridine, which results from the distillation of the former with zinc-dust, Kekulé demonstrated by converting glutaconimide with PCl_5 into *pentachlorpyridine*, identical with an analogous body obtained from pyridine.

With these facts as bases, Kekulé held it as highly improbable that the nitrogen of pyridine was joined to the three carbon atoms α, α_1, γ, as required by Riedel's formula, whereas the Körner formula is in complete harmony with the experimental results, and is supported by them.

The centric formula of pyridine, in which the "central linkages" are in unstable equilibrium, permits of many transitions and changes without displacement of the double linkage, and therefore isolates pyridine from compounds like glutaconic acid and glutaconimide, which bear close genetic relations to pyridine.

The production of pyridine from piperidine (hexahydropyridine or pentamethylene imine, p. 539) is important in determining its constitution. It results upon heating HCl-pentamethylene diamine or δ-chloramylamine (1, 311):

The same may be said of quinoline and isoquinoline (pp. 541, 554), which are benzopyridines which have been obtained synthetically:



Quinoline — Pyridine Dicarboxylic Acid — Pyridine.

Pyridine and a series of its homologues are produced in the dry distillation of nitrogenous carbon compounds, hence they are present in coal-tar, in the tar from shales, in that from peat (very little), and in bone-oil (compare p. 48). Compare B. **30**, 224, for the occurrence of pyridine in fusel oil.

Anderson (1846) isolated the first pyridine bases from bone-oil. These were more exhaustively investigated in 1879 and in the years following by Weidel and his students; also by Ladenburg and others.

Their presence in bone-oil is due to the reciprocating action of fats (glycerol esters) and substances containing ammonia (albumin, etc.); the acroleïn arising from the first probably condensing with the ammonia to pyridines (see synthetic method 1). Bone-glue, free from fats, does not yield pyridine bases, but mainly pyrrols (p. 456) (B. **13**, 83). At present the pyridine bases are obtained chiefly from coal-tar (A. **247**, 1). They are found in the acid used for the purifying of the tar. They can easily be isolated from it in the form of the "pyridine-base mixture," which at present is employed in Germany for the "denaturation" of spirit.

Synthetic Methods for the Production of Pyridine Derivatives:

1. Alkyl pyridines are formed on heating *aldehyde ammonias* alone or with aldehydes and ketones (A. **59**, 298; **155**, 310; B. **23**, 685, etc.):

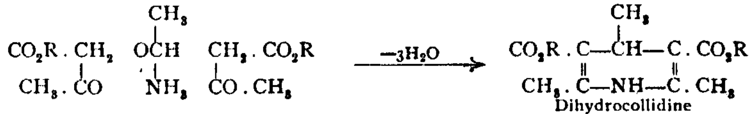
$$CH_3.CHO.NH_3 + 3CH_3.CHO = C_5H_3(CH_3)(C_2H_5)N_2 + 4H_2O$$

α-Methyl-β-ethyl Pyridine (Aldehyde Collidine).

In this reaction evidently several aldehyde molecules condense to unsaturated aldehydes, with long carbon chains, which in turn condense with ammonia, forming rings. *β-Picoline* (p. 532) can also be made by heating glycerol with P_2O_5 and ammoniacal substances—*e.g.*, acetamide, or, better, ammonium phosphate (B. **24**, 1676), when pyrazines are produced as by-products (see these).

2. A method frequently pursued in synthesizing pyridine derivatives consists in the condensation of *β-diketo-compounds* with *aldehydes* and *ammonia* (pyridine syntheses of Hantzsch):

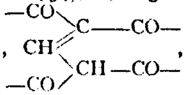
Example a.—Acetoacetic ester (2 mols.), acetaldehyde, and ammonia (or aldehyde ammonia) yield *dihydrocollidine dicarboxylic ester* or 1,3,5-trimethyldihydropyridine dicarboxylic ester, which, by the withdrawal of two hydrogen atoms, may be easily converted into its corresponding pyridine derivative (A. **215**, 1; B. **18**, 2579):



Dihydrocollidine Dicarboxylic Ester.

The acetaldehyde can be replaced by its homologues, by formic aldehyde or benzaldehyde (B. **29**, R. 842), and the second molecule of acetoacetic ester by the 1,3-diketones—*e.g.*, acetyl acetone, benzoyl acetone, etc. (B. **24**, 1669). In the preceding reaction it may be assumed that the aldehyde and acetoacetic ester first combine to ethylidene diacetoacetic ester, $CH_3.CH[CH(CO_2R).COCH_3]_2$. This is a 1,5-diketone derivative, which unites with ammonia to a pyridine ring, just as 1,4-diketones and ammonia form pyrrols (p. 456). Consequently, dihydrocollidine dicarboxylic ester is produced in excellent yield in the condensation of ethylidene acetoacetic ester and β-amidocrotonic acid ester, in that the latter attaches itself to the unsaturated linkage of the former, with consequent ring formation (B. **24**, 1667).

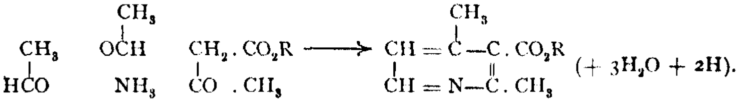
Furthermore, pyridine derivatives are easily obtained by condensing oxymethylene acetoacetic esters with β-amidocrotonic esters (B. **26**, 2734), or, in general, if NH_3 be allowed to act upon 1,5-diketones of the constitution,



, which are prepared by condensing ethoxymethylene acetoacetic ester and analogously constituted compounds with β-ketonic esters or 1,3-diketones (B. **28**, R. 491):

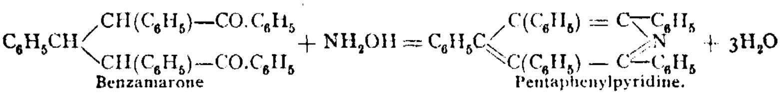
Compare B. **28**, R. 1002, for another explanation of the mechanism of this reaction.

Example b.—1,3-Dimethylpyridine-2-carboxylic ester forms upon digesting acetoacetic ester (1 mol.) with acetaldehyde (2 mols.) and ammonia:



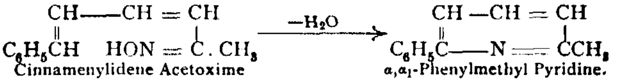
The mechanism of this reaction is probably similar to that in example a. The dihydro-product formed at first is probably oxidized by the excessive aldehyde to the corresponding pyridine. This reaction can also be varied by the use of different aldehydes.

3. 1,5-Diketones, the keto-groups of which are combined with phenyl residues (1,3-dibenzoyl paraffins), yield pyridines when acted upon with hydroxylamine (A. **281**, 36):



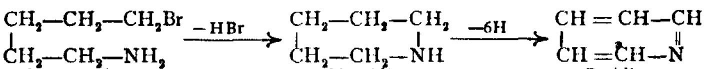
Benzamarone Pentaphenylpyridine.

Pyridines are also produced by the dry distillation of certain oximes of diolefine monoketones (B. **28**, 1726; **29**, 613):



Cinnamenylidene Acetoxime α,α_1-Phenylmethyl Pyridine.

4. Pyridines are produced by oxidizing the synthetic hexahydropyridines, piperidines, or pentamethyleneimides (p. 538) with sulphuric acid or silver acetate (B. **25**, 1621):

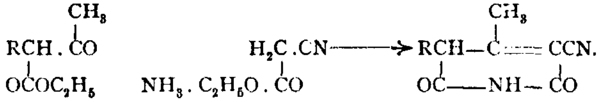


δ-Bromamylamine Piperidine Pyridine.

5. Oxypyridine derivatives (pyridones) result from the action of ammonia upon the pyrone compounds; the linking oxygen atom of the pyrones is replaced by the NH-group.

6. α,α_1-Dioxypyridines, which can also be regarded as imides of glutaconic acid and its homologues, are obtained from glutaconamic acid, etc., by a ring-formation (comp. 1, 467; 11, 527); similarly, *citrazinic acid*, dioxypyridine carboxylic acid, is prepared by the action of ammonia upon aconitic ester; also from citramide (1, 530).

7. Further, glutaconimide derivatives may be made synthetically by condensing aceto-acetic esters and cyanacetic ester with ammonia or primary amines (B. **29**, R. 654; C. 1897, I, 927):



Similarly, α-pyridones are obtained by condensing β-amidoketones—*e. g.*, diacetonamine, $CH_3 . CO . CH_2 . C(CH_3)_2NH_2$, or acetyl acetonamine, $CH_3 . CO . CH : C(CH_3)$-NH_2, with cyanacetic ester (B. **26**, R. 943).

8. The fact that β-chlor- and β-brom-pyridine can by produced by heating potassium pyrrol with $CHCl_3$ and $CHBr_3$ is of interest. Pyrrol and sodium ethylate may be used as a substitute for potassium pyrrol. Pyridine results if CH_2I_2 be used, and with benzal chloride the product is β-phenylpyridine (B. **20**, 191). Alkylpyridines (B. **19**, 2196) are similarly formed from alkylpyrrols upon heating them with concentrated hydrochloric acid. *Compare the conversion of alkyl indols into quinoline derivatives* (p. 544).

Behavior: The pyridine bases are colorless liquids with a peculiar odor. Pyridine is miscible with water. The solubility of the higher members grows rapidly less. Frequently they are more soluble in cold than in hot water. The pyridines are tertiary bases and form crystalline salts with one equivalent of the acids.

1. *Salts.*—The platinum double salts of the formula $(C_5H_5N . HCl)_2$-$PtCl_4$ lose two molecules of hydrochloric acid upon prolonged boiling and form $(C_5H_5N)_2PtCl_4$ (see pyrazoles, p. 482). The pyridines form addition compounds with many inorganic salts. These, with $HgCl_2$ and $AuCl_3$, are characteristic and serve for the separation of the individual bases (A. **247**, I; *comp.* C. *1897, II, 129, 311*).

2. Alkyl iodides and pyridines form *alkyl pyridinium iodides.*

The corresponding alkyl pyridinium hydroxides appear to be very unstable. If they be treated with sodium hydroxide and potassium ferricyanide an atomic rearrangement ensues and n-alkylpyridones result:

(B. **25**, 3326; compare also the quinolinium compounds, p. 545).

3. The pyridines also unite with chloracetic acid and its homologues, with formation of *pyridine betaïnes.*

4. When the alkyl pyridinium iodides are heated to 300° alkyl pyridines result, with a migration of the alkyl-group to α- or γ-C-atom (Ladenburg, B. **17**, 772). This is analogous to the production of homologous anilines from n-alkyl anilines (p. 72).

5 (a). α-Methyl pyridines condense with aldehydes on heating with water; this is in the nature of the aldol formation. The *alkines*, secondary alcohols, result (B. **23**, 2709). Thus, α-picoline and acetaldehyde form α-picolyl methyl alkine, $(C_5H_4N)CH_2$.-$CHOH . CH_3$. The compounds with chloral are especially characteristic (B. **26**, 1414).

5 (b). Pyridines with unsaturated side-chains are formed on heating α-methyl picolines with aldehydes and zinc chloride. Thus, α-picoline and benzaldehyde yield *stilbazole*, $(C_5H_4N)CH : CHC_6H_5$ (p. 533).

6. Oxidizing agents—*e. g.*, nitric acid, chromic acid—as a rule do not attack the pyridines. All the homologous pyridines, on the other

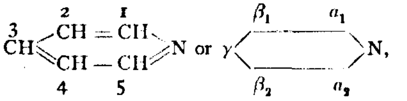
hand, and even the phenyl pyridines are oxidized by potassium permanganate to *pyridine carboxylic acids*, which finally yield pyridine upon distillation with lime.

7. Reducing agents (sodium and alcohol) convert the pyridine bases into *hexahydropyridines*, or piperidines, which can be decomposed by various methods into fatty bodies (compare piperidine decompositions, p. 539). The pyridines are reduced to *paraffins* when heated with hydriodic acid. Pyridine yields pentane.

8. *Halogen*, *nitro-*, and *sulpho*-derivatives are prepared with far more difficulty from the pyridines than from the benzenes.

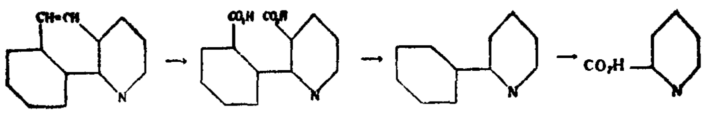
Isomerides.

The derivatives produced by the replacement of the hydrogen atoms in pyridine can easily be deduced in their possible isomerisms from the given structural formulas, and are perfectly analogous to the isomerisms of the benzene derivatives. Representing the five hydrogen atoms, or the affinities of the pyridine nucleus, with numbers or letters, corresponding to the diagram—



then the positions, 1 and 5, also 2 and 4 (as in benzene), are similar (p. 33). The first may be designated the ortho-, the latter, the meta-positions—while the position 3, occurring only once, corresponds to the *para* of benzene. From this we conclude that the mono-derivatives of pyridine, $C_5H_4(X)N$, can exist in three series, while six isomerides are possible with the di-derivatives $C_5H_3(X_2)N$. This is verified by the existence of three methyl, three propyl- and phenyl-pyridines, $C_5H_4(R)N$, of three pyridine-monocarboxylic acids, $C_5H_4(CO_2H)N$, of six dicarboxylic acids, etc. The determination of place for the pyridine derivatives usually follows from their conversion into carboxylic acids of pyridine.

Constitution of the Pyridine Monocarboxylic Acids.—The constitution of pyridine-α-carboxylic acid or picolinic acid and pyridine-β-carboxylic acid or nicotinic acid is evident from its production in the oxidation of α- and β-phenylpyridines. These latter bodies have been obtained from α- and β-naphthoquinoline. When these are oxidized the first products are α- and β-phenylpyridine dicarboxylic acids, which upon the loss of $2CO_2$ become phenylpyridines. This proof of constitution presupposes, therefore, the constitution of α- and β-naphthoquinolines. The diagram represents the derivation of the constitution of picolinic acid:



α-Naphtho-quinoline — α-Phenylpyridine Dicarboxylic Acid — α-Phenyl Pyridine — Pyridine-α-carboxylic Acid, α-Picolinic Acid.

The behavior of the pyridine dicarboxylic acids leads to a simpler deduction of the position of their atoms (B. 18, 2967). Quinolinic acid (pyridine dicarboxylic acid), formed by the oxidation of quinoline, has the position (1,2), and cinchomeronic acid, from isoquinoline, has the position (2,3). Quinolinic acid loses one molecule of carbon dioxide when heated and forms nicotinic acid, while cinchomeronic acid yields nicotinic acid and isonicotinic acid; therefore nicotinic acid is $\beta = 2$ and isonicotinic acid $\gamma = 3$.

Pyridine, C_5H_5N, boiling at 114.8°, with sp. gr. 1.003 (0°), can be prepared from bone-oil, and is obtained from all the pyridine-carboxylic acids on distillation with lime. Its hydrochloride, $C_5H_5N . HCl$, is

deliquescent, and with platinum chloride it forms a double salt, $(C_5H_5N.HCl)_2PtCl_4$, melting at 240°. See B. **29**, R. 295, for pyridine mercury compounds. Its *iodmethylate* melts at 117° (B. **29**, R. 994). *Pyridine betaïne*, $C_5H_5N\Big\langle\begin{array}{l}CH_2CO\\ \quad\;\; |\\ \quad\;\; O\end{array}$, melting with decomposition at 150°, is formed by the interaction of pyridine and chloracetic acid (B. **23**, 2609). Compare I, 521; B. **26**, R. 54, for the action of pyridine upon acetyl chloride and benzoyl chloride. Sodium and alcohol reduce it to piperidine, while normal pentane is produced when it is heated with hydriodic acid.

1. **Homologous Pyridines. Methyl Pyridines,** $C_5H_4(CH_3)N$, **Picolines** (from *pix*, tar; because they were obtained from coal-tar):

a-**Picoline** boils at 130°; its sp. gr. is 0.965 at 0°, and it is oxidized by potassium permanganate to picolinic acid. *β*-**Picoline** boils at 143°; its sp. gr. is 0.977. It is formed when strychnine is distilled (B. **23**, 3555), and upon heating glycerol with P_2O_5 and ammonium phosphate; also by heating trimethylenediamine hydrochloride (B. **23**, 2730). It yields nicotinic acid on oxidation. *γ*-**Picoline** boils at 144°. Its sp. gr. is 0.974 at 0°. It has also been prepared by heating pyridine iodmethylate (p. 531). It yields isonicotinic acid when it is oxidized.

Dimethyl Pyridines, *Lutidines*, $C_5(CH_3)_2H_3N$. Bone-oil contains mainly: *aa₁-Lutidine*, boiling at 142°, with sp. gr. 0.942; *a,γ-Lutidine*, boiling at 157°, with sp. gr. 0.9493; and *β,γ-Lutidine*, boiling at 164° (B. **21**, 1006; **29**, 2996). *β,β₁-Lutidine*, from the corresponding carboxylic acid, boils at 170° (B. **23**, 1113).

a-**Ethyl Pyridine,** $C_5H_4(C_2H_5)N$, boils at 148°; its sp. gr. is 0.949 at 0°. *γ*-**Ethyl Pyridine** boils at 165°; its sp. gr. is 0.952 at 0°. These two compounds result upon heating pyridine ethyl iodide. *β*-**Ethyl Pyridine** has been obtained, together with the *γ*-body, from cinchonine and brucine on heating with caustic potash. It boils at 166°.

Sym. (1,3,5) *Trimethyl Pyridine*, $C_5H_2(CH_3)_3N$, collidine, is obtained from synthetic dihydrocollidine dicarboxylic ester (p. 528) by oxidation, saponification, and the elimination of carbon dioxide. It boils at 172°. **1,3,4-Collidine,** boiling at 165–168°, occurs in coal-tar (B. **29**, 2998).

(1,4)-**Methyl-Ethyl Pyridine,** $C_5H_3(CH_3)(C_2H_5)N$, has been prepared from various aldehyde compounds, hence called *aldehydine* or *aldehydcollidine*. It boils at 178°.

a-**Propyl Pyridine, Conyrine,** $C_5(C_3H_7)H_4N$, is produced on heating conine with zinc-dust. It boils at 167°.

a-**Isopropyl Pyridine** is produced, together with the *γ*-compound, when pyridine propyl iodide or isopropyl iodide is heated. It boils at 158°.

Parvuline, v-Tetramethyl Pyridine, boiling at 227-230°, occurs in coal-tar (B. **28**, 796).

β,β₁-**Dibenzyl Pyridine,** $C_5H_3(C_7H_7)_2N$, boiling at 89°, is formed in the condensation of benzaldehyde with benzoyl piperidine (p. 540) (A. **280**, 36).

a- and *β*-**Phenyl Pyridine,** $C_5(C_6H_5)H_4N$, boiling at 269° and 270°, result from the elimination of $2CO_2$ from their carboxylic acids, the decomposition products of *a*- and *β*-naphthoquinoline. The *a*-body can also be made by heating the corresponding *a*-pyridone with zinc-dust (B. **29**, 1678).

p-Nitrophenyl Pyridine, melting at 117°, is obtained from nitrosodiazobenzene and pyridine. By reduction it yields p-amidophenylpyridine, melting at 102°, which yields *a*-phenyl pyridine (B. **29**, 167). **Dinitrophenyl Pyridine** melts at 118° (B. **29**, 279). *γ*-**Phenyl Pyridine,** melting at 77° and boiling at 274°, results from a transposition of the condensation product of acetoacetic ester with benzaldehyde and ammonia (p. 528).

a,a₁-**Phenyl Methyl Pyridine,** $C_5(C_6H_5)(CH_3)H_3N$, boiling at 281°, is obtained from cinnamylidene acetoxime (p. 529 and B. **28**, 1727). *a,a₁*-**Diphenyl Pyridine,** melting at 82°, has been obtained (1) by distilling the oxime of cinnamylene-acetophenone (method 3, p. 529); (2) from *a,a₁*-diphenyl-*γ*-pyridine-carboxylic acid, produced on heating diphenacyl-malonic acid with ammonia; and (3) by oxidizing *a*-phenyl-

naphthocinchoninic acid (B. **29**, 798; **30**, 1499) **Tetra- and Pentaphenyl Pyridines**, melting at 179° and 240°, are produced from desoxybenzoïn benzylidene acetophenone, and from benzamarone and NH_2OH (p. 529) (A. **281**, 50; B. **26**, 440).

γ-γ-**Dipyridyl**, $(C_5H_4N)_2 + 2H_2O$, melting at 73° (114°) and boiling at 305°, is produced, together with an oily, polymeric pyridine $(C_5H_5N)x$, when sodium acts upon pyridine (B. **24**, 1478). β,β₁-**Dipyridyl**, melting at 68° and boiling at 287°, is obtained from its dicarboxylic acid, an oxidation product of phenanthroline (p. 554). Compare B. **21**, 1077, for another dipyridyl.

Vinyl Pyridine, $C_5H_4(C_2H_3)N$, results when pyridine vapors are conducted, together with ethylene, through a tube heated to redness, as well as from α picolyl alkine by the loss of water, and from pyridyl-β-brompropionic acid (p. 538) by the exit of CO_2 and HBr. It boils at 160° (B. **20**, 1644; A. **265**, 229).

α-**Allyl Pyridine**, $C_5H_4(C_3H_5)N$, is produced when picoline and paraldehyde are heated to 200° (A. **247**, 26). It boils at 290°. Sodium and alcohol convert it into propyl piperidine (inactive conine, p. 562).

Styryl Pyridine, *Stilbazole*, $C_5(CH:CHC_6H_5)H_4N$, melting at 61° and boiling at 325°, is formed from α-picoline with benzaldehyde and zinc chloride.

2. **Halogen Pyridines**: The pyridines containing halogens in the nucleus are obtained with difficulty by the direct action of the halogens upon the pyridines. Bromine particularly replaces the alkyl group in the homologous pyridines very easily (B. **25**, 2985; **28**, 1759). The replacement of the pyridine hydrogen atoms is more easily effected upon heating pyridine or the oxypyridines with phosphorus or antimony pentachlorides.

α-**Chlor-pyridine**, melting at 166°, results on treating α-oxypyridine with PCl_5. β-**Chlor-pyridine**, boiling at 148°, and β-**Brom-pyridine**, boiling at 170°, are formed when CCl_3H or CBr_3H acts upon pyrrol-potassium (p. 530). α **Phenyl-α-chlor-pyridine**, melting at 34°, is obtained from phenylpyridone (B. **29**, 1679). **Dichlor-pyridine**, melting at 67°, and **trichlor-pyridine**, melting at 50°, result from the action of PCl_5 upon barium pyridine disulphonate. α,γ-**Dichlor-picoline**, boiling at 206°, is obtained from dioxypicoline (B. **28**, R. 644). **Tetrachlor-pyridine**, melting at 80–85°, and **Pentachlor-pyridine**, C_5Cl_5N, melting at 124–125°, are prepared from pyridine and phosphorus pentachloride. The same reagent converts dioxypyridine (glutaconimide) into perchlorpyridine (Kekulé, p. 527).

3. **Pyridine Sulphonic Acids** are formed, together with pyridine, on heating piperidine with concentrated sulphuric acid.

β-**Pyridine Sulphonic Acid**, $C_5H_4(SO_3H)N$, also results on treating pyridine with sulphuric acid. β-Cyan-pyridine, melting at 49°, is formed when its sodium salt is distilled with potassium cyanide. It is the nitrile of nicotinic acid (p. 536) and yields β-oxypyridine on fusion with caustic potash.

4. **Nitro-pyridines**: Nitration of the pyridine nucleus seems only possible when NH_2-, OH-, or similar groups are present, which, as in the case of benzene, facilitate the nitration (p. 149).

The *nitration of β-oxypyridine* (p. 534) *in the form of its acetyl ester with nitric acid* containing N_2O_3 gives rise to two **nitro-oxypyridines**, melting at 211° and at 295–298° with decomposition; also a **dinitro-oxypyridine**, melting at 133° (B. **28**, R. 911). See *nicotinic acid* (p. 536) *for the* **nitroamidonicotinic acids.**

5. **Amido-pyridines** have been obtained from the pyridine acid-amides with bromine and caustic potash (Hofmann's reaction), and also by the exit of CO_2 from amidopyridine carboxylic acids.

α-**Amido-pyridine**, melting at 56° and boiling at 204°, is obtained from the amide of α-picolinic acid; also from α- and α₁-amido-nicotinic acid (B. **27**, 1317, R. 410; A. **288**, 253). β-**Amido-pyridine**, melting at 64° and boiling at 251°, is formed in the action of bromine and caustic potash upon the amide of nicotinic acid (B. **28**, R. 322). γ-**Amido-α,α₁-lutidine**, $C_5H_2(CH_3)_2(NH_2)N$, melting at 186° and boiling at 246°, is obtained from amido-lutidine dicarboxylic acid (B. **27**, 1325). Chlorinated α-amidopyridines have been obtained by the action of PCl_5 upon β-oxyglutaramide. **Trichlor-α-amido-pyridine**, $C_5HCl_3(NH_2)N$, melts at 143–144°.

6. **Oxypyridines**: They correspond to the amidophenols, as they form salts both with bases and acids. They are formed with special ease from the oxypyridine carboxylic

acids by the elimination of the carboxyl groups. The most of these acids have been produced by the action of ammonia upon the corresponding pyrone derivatives. Ferric chloride imparts a red color to nearly all their solutions. On the other hand, the *a*- and *γ*-oxypyridines manifest the deportment of cyclic imides or lactams. They must be viewed as *keto* or *oxo*-compounds of the hydropyridines, and are called, therefore, ***pyridones***. The following formulas have been considered for the *a*- and *γ*-monoxypyridines:

$$\text{I. } CH\langle{}^{CH - C(OH)}_{CH = CH\text{——}}\rangle N \qquad C(OH)\langle{}^{CH - CH}_{CH = CH}\rangle N$$

a-Oxypyridine — γ-Oxypyridine

$$\text{II. } CH\langle{}^{CH - CH}_{CH = CH}\rangle NH \qquad CO\langle{}^{CH = CH}_{CH = CH}\rangle NH$$

a-Pyridone — γ-Pyridone.

Although it is undetermined which of the two possible representations belongs to the free oxy-bodies, alkyl derivatives are obtained from both in which the alkyl residue replaces the imide or hydroxyl hydrogen (B. 24, 3144) (1, 363). The following formulas should also be considered for the a,a_1 dioxypyridines or glutaconimides:

$$\text{I. } CH\langle{}^{CH-C(OH)}_{CH=C(OH)}\rangle N \quad \text{II. } CH\langle{}^{CH-CO}_{CH=C(OH)}\rangle NH \quad \text{III. } CH\langle{}^{CH-CO}_{CH_2-CO}\rangle NH.$$

(Compare the pyrazolons, the isoxazolons, benzimidazolons, indoxyl, isatin, etc.)

(1) *Monoxypyridines:* **1-Oxypyridine,** *a*-**Pyridone,** C_5H_5ON, melting at 106° and boiling at 281°, is obtained from oxyquinolinic acid (p. 537) and from oxy-nicotinic acid. Bromine water converts it into a dibromoxpyridine, $C_5H_2Br_2(OH)N$, melting at 206°. With ethyl iodide it yields *n-ethyl-a-pyridone*, $CH\langle{}^{CH - CO}_{CH = CH}\rangle N . C_2H_5$, boiling at 247°, while the silver salt of *a*-oxypyridine and the same reagent yield *a-ethoxy-pyridine*, $CH\langle{}^{CH - C(OC_2H_5)}_{CH = CH\text{——}}\rangle N$, boiling at 156°. *a-Methoxypyridine* can also be prepared from *a*-pyridone and diazomethane (p. 445; B. 28, 1625).

1,3-Dimethyl-*a*-pyridone, *Pseudolutidostyril, Mesitene Lactam,* melting at 180°, results from the action of ammonia upon dimethyl coumalin or mesitene lactone (p. 522), as well as from its carboxylic acids (1, 363). *a*-**Phenyl Pyridone,** melting at 197°, is formed from phenyl coumalin and ammonium acetate. With aniline it yields ***a*,n-diphenylpyridone,** melting at 145° (B. 29, 1677).

2-Oxypyridone, $C_5H_4(OH)N$, melting at 124°, distils without decomposition. It is produced when *β*-pyridine sulphonic acid is fused with caustic potash (B. 28, R. 911), or by the action of nitrous acid upon *β*-amidopyridine. Its ethyl ether, $C_5H_4(OC_2H_5)N$, results from the interaction of *β*-brompyridine and alcoholic potash.

3-Oxypyridine, *γ*-**Pyridone,** $C_5H_5ON(+ H_2O)$, melting at 148°, is produced by heating oxypicolinic acid and ammon-chelidonic acid. Methyl iodide converts it into the hydroiodide of n-methyl-*γ*-pyridone, $OC\langle{}^{CH - CH}_{CH = CH}\rangle NCH_3$, melting at 89°. *γ-Methoxy-pyridine*, $(CH_3O)C\langle{}^{CH - CH}_{CH = CH}\rangle N$, is isomeric with it. This compound may be prepared by heating *γ*-chlorpyridine with sodium ethylate. It boils at 190°, and, unlike its isomeride, is broken down, when heated with hydriodic acid, into methyl iodide and *γ*-pyridone.

2,4-Dimethyl-3-oxypyridine, *γ*-**Lutidone,** $C_5(CH_3)_2H_2ON(+ 1\frac{1}{2}H_2O)$, melting at 225°, is obtained from lutidone dicarboxylic acid (p. 538), as well as from dihydracetic acid (p. 521) on heating with ammonia (B. 28, R. 644). *γ*-**Ethoxylutidine,** boiling at 207°, results upon diazotizing *γ*-amidolutidine (p. 533) in alcoholic solution (B. 27, 1328).

(2) *Dioxypyridines:* **1,5-Dioxypyridine,** *glutaconimide*, $C_5H_5O_2N$ (1, 467), melting at 183–184°, is obtained from oxyglutarimide, glutaconamic acid, or glutacondiamide. Its salts (*chloride*, $+ H_2O$; *sulphate*, $+ 2H_2O$) are decomposed by much water. It

yields pyridine upon distillation with zinc-dust. Phosphorus pentachloride converts it into *pentachlorpyridine* (compare p. 527).

2-Methyl-1,5-dioxypyridine, $C_5(CH_3)H_4O_2N$, melting at 191°, **2-Ethyl-1,2-Benzyl-dioxypyridine**, etc., have been prepared by the action of ammonia upon methyl-, ethyl-, and benzyl-glutaconic esters (B. **26**, R. 318, 587). These dioxypyridines correspond to resorcinol of the benzene series, and like it they form *dyes* with phthalic anhydride (see p. 364 and B. **26**, 1559).

Consult B. **25**, R. 793; **28**, R. 644, for **1,3-dioxypicoline.**

Different isomeric dioxypyridines have, furthermore, been prepared by the fusion of pyridine disulphonic acids with caustic potash (B. **17**, 1832) and by the removal of CO_2 from comenamic or dioxypicolinic acid (p. 538) (B. **18**, R. 633), etc.

(3) *Trioxypyridines:* **1,3,5-Trioxypyridine,** *Triketopiperidine*, $C_5H_5O_3N$, decomposes at 220–230°. It corresponds to phloroglucin (p. 165). It can be obtained by boiling glutazine with hydrochloric acid. Heated with ammonia it reforms **Glutazine,** *β-Imido-glutarimide*, $NH:C\begin{smallmatrix}\diagup CH_2-CO\diagdown\\ \diagdown CH_2-CO\diagup\end{smallmatrix}NH$ (?), melting with decomposition at 300°, which may be prepared by heating acetone dicarboxylic ester with ammonia (B. **20**, 2655).

Pyromecazonic Acid is an isomeric trioxypyridine, obtained from pyromeconic acid with ammonia. Ferric chloride colors it a dark indigo-blue.

7. **Pyridyl Alcohols:** These are sometimes called *pyridyl alkines*. They arise (1) in the aldol condensation of *α*-methyl pyridines with aldehydes on boiling with water; (2) from their HBr-esters, the homologous pyridines brominated in the side-chain; (3) by the reduction of the corresponding ketones:

1-Picolyl Alkine, $C_5H_4N(CH_2.CH_2OH)$, boiling at 179° (22 mm.), and **1-Picolyl Methyl Alkine,** $C_5H_4NCH_2(CHOH)CH_3$, are obtained from *α*-picoline with formic and acetaldehydes (B. **22**, 2583; **23**, 2709, 2725). **1-Picolyl Trichlor-methyl Alkine,** $C_5H_4NCH_2CH(OH)CCl_3$, melting at 87°, is formed from *α*-picoline and chloral. Alcoholic potash converts it into *α-pyridyl acrylic acid* (p. 538). **Pyridyl-*α*-ethyl Alkine,** $C_5H_4NCH(OH)C_2H_5$, boiling at 213° to 218°, is isomeric with *α*-picolylmethyl alkine. It is made by reducing pyridyl ethyl ketone with sodium amalgam. **1-Picolyl-4-methyl Alkine,** $C_5H_3(CH_3)NCH(OH)CH_3$, boiling at 240°, results upon boiling bromcollidine with water (B. **28**, 1759).

8. **Pyridyl Ketones:** Ketones of the pyridine series are obtained in the distillation of pyridine carboxylic acids with fatty or aromatic acids (Engler, B. **24**, 2525). They yield secondary alcohols, together with pinacones, by reduction.

1-Pyridyl Methyl Ketone, $(CH_3CO)C_5H_4N$, boiling at 192°, is prepared from calcium picolinate and acetate. Its *oxime* melts at 120°. Its *phenylhydrazone* melts at 155°.

2-Pyridyl Methyl Ketone, boiling at 220°, is obtained from calcium nicotinate and acetate. **1-Picoline-4-methyl Ketone,** $C_5H_3(CH_3)(COCH_3)N$, boiling at 233°, results upon oxidizing the corresponding alkine (B. **28**, 1764).

1-Pyridyl Ethyl Ketone, $(C_2H_5CO)C_5H_4N$, boiling at 205°, is changed by sodium and amyl alcohol to *α-ethyl piperyl alkine*, $C_2H_5CH(OH).C_5H_9NH$, which is identical with the *pseudoconhydrin*, present in the conine alkaloids.

2-Phenyl Pyridyl Ketone, $C_6H_5CO.C_5H_4N$, boiling at 307° (B. **20**, 1209), forms two isomeric *oximes*, melting at 142° and 162° (B. **29**, R. 832). **β,γ-Diacetyl-*α*,*α*₁-lutidine,** $C_5H(COCH_3)_2(CH_3)_2N$, is produced by the action of ammonia upon methenyl-bisacetylacetone, $(CH_3CO)_2CH.CH:C(COCH_3)_2$—compare 1, 478). **1-Acetacetyl Pyridine,** $(C_5H_4N)CO.CH_2.CO.CH_3$, melting at 50° and boiling at 137–143° (15 mm.), is obtained from picolinic ester, acetone, and sodium ethylate (B. **29**, R. 846).

9. **Pyridine Carboxylic Acids.**—These acids of pyridine result upon oxidizing the homologous pyridines with potassium permanganate, when alkyl as well as phenyl groups are converted into carboxyl. The condensed pyridine derivatives—*e.g.*, quinoline, isoquinoline, etc.—are similarly decomposed, the benzene rings being ruptured and oxidized to carboxyl. Hence, most alkaloids, being pyridine derivatives, yield these acids upon energetic oxidation.

The lower acids can be prepared from the pyridine polycarboxylic acids by heating them with hydrochloric acid. Usually, in this treatment it is the COOH groups, occupying the α-position, which are split off. Upon heating with lime all the carboxyl groups are eliminated and pyridine is formed.

The pyridine carboxylic acids, like the other pyridine derivatives, are reduced by sodium and alcohol to piperidine carboxylic acids.

A number of pyridine carboxylic acids are reduced by sodium amalgam in aqueous-alkaline solution to *lactonic acids* of the fatty series. The group —CH = N — CH = is then converted into —CO—O—CH_2— (B. **25**, R. 904; **26**, R. 8; **27**, R. 193, etc.).

As the pyridines are bases, their acids manifest the character of amido-acids. The basic properties disappear with the polycarboxylic acids.

The methods of determining position or place in the monocarboxylic acids have been given on p. 531. Of the dicarboxylic acids, quinolinic acid, because of its formation from quinoline (p. 527), must be the α,β-dicarboxylic acid, and cinchomeronic acid, because of its production from isoquinoline (p. 554), must be the β,γ-dicarboxylic acid.

A. *Pyridine-mono-carboxylic Acids:*

1-**Pyridine Carboxylic Acid, Picolinic Acid,** $C_5H_4N(CO_2H)$, is obtained by the oxidation of α-picoline. It melts at 135–136°, and sublimes. Ferrous sulphate imparts to its solutions, as well as to those of all pyridine carboxylic acids having the carboxyl group in the α-position, a *yellow-red* color.

2-**Pyridine Carboxylic Acid, Nicotinic Acid,** was first obtained by oxidizing nicotine. It is also prepared from β-picoline, as well as from β-cyanpyridine. It melts at 228–229°. Its iodmethylate forms a *betaïne*, $C_5H_4(COO)N \cdot CH_3$, which is identical with the alkaloid *trigonelline* (p. 564). 5-**Chlornicotinic Acid,** melting at 199°, is obtained from oxynicotinic acid, and when heated with ammonia becomes 5-**Amidonicotinic Acid,** which changes to α-amidopyridine on heating, and by nitration yields 4,5-**nitroamidonicotinic acid,** melting at 280°. The reduction of the latter yields 4,5-**diamidonicotinic acid.** 1-**Amidonicotinic Acid,** from quinolinamic acid, also yields α-amidopyridine on the application of heat, and by nitration becomes **nitroamidonicotinic acid** (B. **27**, 1317; A. **288**, 253).

3-**Pyridine-carboxylic Acid, Isonicotinic Acid,** is obtained from γ-methyl pyridine, or from cinchomeronic acid, by the splitting-off of CO_2. It melts at 304°.

Homologous Pyridine Monocarboxylic Acids:

3-**Methyl-1-pyridine Carboxylic Acid** is obtained on heating uvitonic acid when $1CO_2$ splits off. It sublimes without previously fusing.

3-**Methyl-nicotinic Acid** results on heating methyl quinolinic acid. It melts at 210°.

1,3-**Dimethyl-nicotinic Acid,** $C_5H_2(CH_3)_2N(CO_2H)$. Its *ethyl ester* results in the condensation of acetoacetic ester with aldehyde and aldehyde-ammonia. The free acid contains two molecules of water of crystallization.

B. *Pyridine Dicarboxylic Acids:*

1,2-**Pyridine Dicarboxylic Acid, Quinolinic Acid,** $C_5H_3N(COOH)_2$, melting at 190° with decomposition, is obtained from quinoline and from 1- and 2-methyl-quinoline by oxidation with potassium permanganate (B. **19**, 293). The oxidation of p-oxyquinoline with bleaching lime yields an intermediate product, *carbopyridyl glyceric acid,* $C_5H_3N<^{COOH}_{CH(OH).CH(OH)COOH}$, which changes with ease to *acetonicotinic acid,* $C_5H_3N<^{COOH}_{COCH_3}$ (compare B. **26**, 1501, and decomposition of β-naphthol and naphthoquinone, pp. 392, 393).

The **anhydride** melts at 134° and the **imide** at 230° (A. **288**, 257).

2,3-**Pyridine Carboxylic Acid, Cinchomeronic Acid,** is obtained from cinchonine

and cinchonidine by oxidation with nitric acid and by the oxidation of isoquinoline with potassium permanganate. It melts at 266° with decomposition. It yields an *anhydride*, $C_5H_3N(CO)_2O$, melting at 67°. Sodium amalgam reduces it to cinchonic acid, $C_7H_6O_5$, which breaks up into CO_2, and *hydrocinchonic acid* or dimethyl maleic anhydride on application of heat (B. **18**, 2968; **1**, 465).

The methyl betaïne of cinchomeronic acid is **Apophyllenic Acid.**

1,3-Pyridine Dicarboxylic Acid, Lutidinic Acid, $C_5H_3N(COOH)_2 + 2H_2O$, melts at 235° (A. **247**, 37). **1,4-Pyridine Dicarboxylic Acid,** *isocinchomeronic acid*, crystallizing with 1-1½ mols. of water, melts at 236° (B. **19**, 1311).

1,5-Pyridine Dicarboxylic Acid, Dipicolinic Acid, melts at 225° (A. **247**, 33).
2,4-Pyridine Dicarboxylic Acid, Dinicotinic Acid, melts at 314° (B. **19**, 286).

Homologous Pyridine Dicarboxylic Acids:

3-Methyl-quinolinic Acid, $C_5H_2(CH_3)N(CO_2H)_2$, is produced upon oxidizing γ-methyl-quinoline with potassium permanganate. It melts about 186° with decomposition.

1-Methylpyridine-5,3-dicarboxylic Acid, Uvitonic Acid, $C_5(CH_3)H_2N(COOH)_2$, is formed when alcoholic ammonia acts upon pyroracemic acid. It melts at 244°.

Lutidine Dicarboxylic Acid, 1,5-Dimethyl-2,4-pyridine Dicarboxylic Acid, $C_5H(CH_3)_2N(COOH)_2$, melting at 316°, is formed from methenylbisacetacetic ester and ammonia (compare 1, 483, and A. **241**, 31).

(1,3,5)-Trimethyl-pyridine-(2,4)-dicarboxylic Acid, *Collidine Dicarboxylic Acid*, $C_5(CH_3)_3N(CO_2H)_2$. The *diethyl ester* is prepared by the oxidation of dihydro-collidine dicarboxylic ester in alcoholic solution with nitrous acid. It is the starting-out substance for the preparation of a series of higher and lower pyridine carboxylic acids.

C. *Pyridine Tricarboxylic Acids:* **1,2,3-Pyridine Tricarboxylic Acid,** *Carbo-cinchomeronic Acid*, $C_5H_2N(COOH)_3 + 1½H_2O$, melting at 250°, results upon oxidizing quinine, cinchonine (p. 572), various decomposition products of these alkaloids, and γ-methyl quinolinic acid, etc., with potassium permanganate. Consult C. 1897, II, 308, for the esterification of this acid. **1,3,5-Pyridine Tricarboxylic Acid,** melting with decomposition at 145°, is obtained from symmetrical collidine (p. 532) or from uvitonic acid (A. **228**, 29). **1,3,4-Pyridine Tricarboxylic Acid,** *Berberonic Acid*, obtained by the action of nitric acid upon the alkaloid berberine, melts at 235° (B. **25**, R. 582). **1,2,5-Pyridine Tricarboxylic Acid,** (+ $2H_2O$), decomposes at 130° (B. **19**, 1309).

D. *Pyridine Tetracarboxylic Acids:* **1,2,3,5-Pyridine Tetracarboxylic Acid,** $C_5HN(COOH)_4(+ 2H_2O)$, melting at 227°, is obtained from collidine carboxylic acids, or from *flavenol* (p. 546), a quinoline derivative (B. **17**, 2927). Consult B. **19**, 1309, for the 1,2,4,5-*acid*, etc.

E. **Pyridine Pentacarboxylic Acid,** $C_5N(CO_2H)_5 + 2H_2O$, decomposing at 220°, is formed by the oxidation of collidine dicarboxylic acids.

8. Oxypyridine Carboxylic Acids:

The views expressed on p. 534 relative to the oxypyridines or pyridones apply to the constitution of the oxypyridine carboxylic acids. The latter are obtained with remarkable ease from the corresponding pyrone carboxylic acids by the action of ammonia. When heated they break down, as a rule, quite readily into carbon dioxide and pyridones.

A. *Monoxypyridine Carboxylic Acids:* **1-Oxypyridine-4-carboxylic Acid,** *Oxynicotinic Acid*, $C_5H_4ON(COOH)$, melting at 303°, is produced when ammonia acts upon coumalic acid ester, and by the elimination of carbon dioxide from oxyquinolinic acid.

1-Oxypyridine-2-carboxylic Acid, melting with decomposition at 255°, is made from 1-amidonicotinic acid (p. 536), and in various other ways (A. **288**, 265; M. **9**, 145). **3-Oxypyridine-1-carboxylic Acid,** *Oxypicolinic Acid*, (+ H_2O), melting at 250°, is produced by the action of ammonia upon comanic acid (p. 522). **1-Oxypyridine-4,5-dicarboxylic Acid,** *Oxyquinolinic Acid*, $C_5H_3ON(COOH)_2$, decomposing at 254°, is obtained from quinolinic acid by the potash fusion, or from its methyl ether, ***methoxyquinolinic acid***, melting at 140°, which results when potassium permanganate acts upon amidocarbostyril ether. **3-Oxypyridine-1,5-dicarboxylic Acid,** *Ammonchelidonic Acid, Chelidamic Acid*, is obtained by the action of ammonia upon chelidonic acid (p. 522).

1,3-Dimethyl-5-pyridone Carboxylic Acid, *Pseudolutidostyril Carboxylic Acid*, $C_5(CH_3)_2H_2ON(COOH)$, results upon heating HCl-β-amidocrotonic ester to 130° (B. 24, R. 632). **n-Phenyl Lutidone Carboxylic Acid**, $C_5H(CH_3)_2(C_6H_5)ON(COOH)$, is similarly produced, together with γ-oxyquinaldine, upon heating β-anilidocrotonic ester. **1,5-Lutidone-2,4-dicarboxylic Acid**, $C_5(CH_3)_2HON(COOH)_2$, melting at 267°, results when ammonia acts upon dimethyl pyrone dicarboxylic ester. Pentachloride of phosphorus converts it into **3-chlorlutidine dicarboxylic acid**, melting at 224°, which yields **3-amidolutidine dicarboxylic acid** with ammonia at 130° (B. 27, 1323).

B. **Dioxypyridine Carboxylic Acids**: **Dioxypicolinic Acid**, $C_5H_4O_2N(COOH)$. *Comenamic Acid*, is derived from comenic acid (p. 522) by aid of ammonia.

1,5-Dioxyisonicotinic Acid, *Citrazinic Acid*, is formed when citramide, $CONH_2C(OH)<\begin{matrix}CH_2.CONH_2\\CH_2.CONH_2\end{matrix}$, is heated with concentrated sulphuric acid.

An **aldehyde dicarboxylic acid**, $C_5H_2O_2N(COOH)_2(CHO)$ (B. 29, R. 1105), is obtained in the action of chloroform and caustic potash upon citrazinic acid.

9. Pyridyl substituted acids of the fatty series are not very numerous. Certain **pyridyl lactic acids**, because of their relations to the alkaloids, have been investigated:

α,2-**Pyridyl Lactic Acid**, $C_5H_4N.C(OH)(CH_3)COOH$, is formed, along with trimethylamine, in the decomposition of the alkaloid *pilocarpine* (p. 564). Phosphorus tribromide converts it into **pyridyl brompropionic acid**, $C_5H_4NCBrCH_3.COOH$. The homologous **picoline-α-lactic acid**, $[C_5(CH_3)H_3N]C(OH)(CH_3)COOH$, is obtained by saponifying its *nitrile*, the cyanhydrin of picolylmethylketone (p. 535) (B. 28, 1765). β,1-**Pyridyl-lactic Acid**, $C_5H_4N.CH_2CH(OH)COOH$, melting at 125°, is prepared by decomposing its *ortho-chloride*, trichlormethyl picolylalkine, $C_5H_4NCH_2CH(OH)CCl_3$ (p. 535), with soda, whereas with alcoholic potash the product is—

Pyridyl-α-acrylic Acid, $C_5H_4N.CH:CH.COOH$. Bromine converts this acid into *pyridyldibrompropionic acid*, and hydrobromic acid changes it to *pyridylmonobromopropionic acid*, $C_5H_4.CHBr.CH_2.COOH$ (A. 265, 221). *α*,2-**Picoline Acrylic Acid**, $[C_5(CH_3)H_3N]CH(:CH_2)COOH$, is obtained from picoline brompropionic acid, the reaction product of PBr_3 and picoline lactic acid.

HYDROPYRIDINE DERIVATIVES.

Hydropyridines, and, indeed, the perhydrogenized products,—the *piperidines*,—are produced when the pyridines are reduced with zinc and hydrochloric acid, or, better, with sodium and boiling alcohols, and by electrolysis (B. 29, R. 1122; C. 1897, I, 388).

a. Hantzsch obtained *dihydropyridine* derivatives in the pyridine syntheses from acetoacetic ester and aldehyde ammonias. They part very readily with two atoms of hydrogen and revert to pyridines. Further, several dihydropyridines have been obtained as liquids, with penetrating odor and easily resinified, by the action of caustic potash upon alkylpyridinium iodides (B. 14, 1497).

b. *Tetrahydropyridines, Piperideïnes*: **Tetrahydropicoline**, $C_5H_8(CH_3)N$, boiling at 132°, is obtained from δ-amidobutylmethyl ketone by ring-formation (B. 25, 2190; A. 294, 135):

$$\begin{matrix}CH_2.CH_2.NH_2\\|\\CH_2.CH_2.CO.CH_3\end{matrix} \longrightarrow \begin{matrix}CH_2.CH_2.NH\\|\qquad\qquad|\\CH_2.CH:CCH_3\end{matrix}.$$

The tetrahydropyridines include a series of bases, which have been prepared from the piperidines by the action of bromine and sodium hydrate, or iodine and silver oxide, or by the exit of water from the oxypiperidines. Thus, the **coniceïnes** result from the action of phosphorus pentoxide upon conhydrin (p. 562).

The n-alkyl derivatives of the pyridones (p. 534) and the dioxypyridines or glutaconimides are to be viewed as *keto*-derivatives of di- and tetrahydropyridines.

c. *Hexahydropyridines, Piperidines*: **Hexahydropyridine, Piperidine**, *Pentamethyleneimide*, $CH_2<\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}>NH$, boiling at 106°, is a

liquid dissolving quite readily in water and in alcohol. Its odor is like that of pepper. It occurs attached to piperic acid (p. 285) as piperine in pepper, and is produced when piperine is heated together with alcoholic potash. It may be synthesized (1) by heating pentamethylene diamine hydrochloride; (2) by heating ε-chlor- and ε-bromamylamine with caustic potash (previously mentioned); and (3) by the reduction of pyridine, into which it passes when heated with sulphuric acid to 300°, or, better, with nitrobenzene to 260°, or by boiling with silver oxide or silver acetate in glacial acetic acid (B. **25**, 1620).

Decomposition of Piperidine.—The piperidine ring is ruptured in the following reactions:

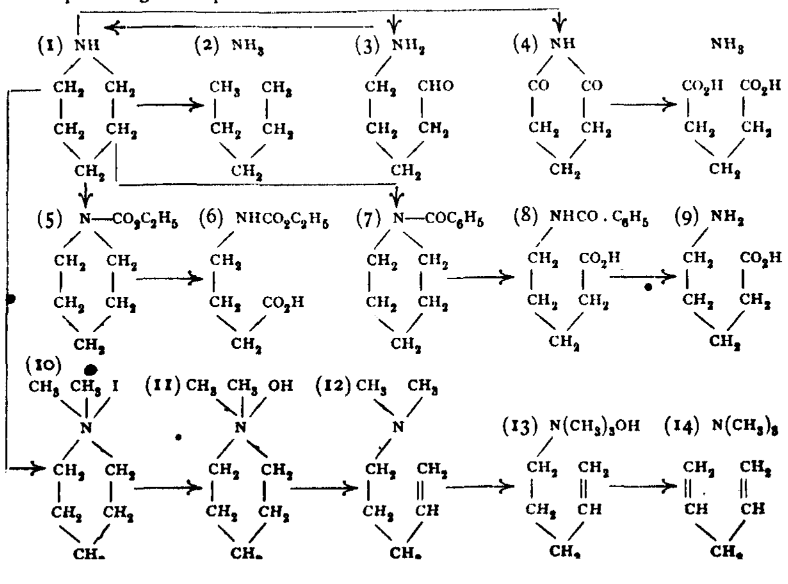
1. When piperidine (1) is heated to 300° with hydriodic acid it is converted into ammonia and n-pentane.

2. When piperidine is oxidized with hydrogen peroxide it changes to δ-amidovaleric aldehyde (3) and n-glutarimide (4). The decomposition by means of hydrogen peroxide with the formation of δ-amidoaldehydes is observed also with the homologous piperidines. The δ-amidoaldehydes regenerate the piperidines with caustic potash, and with sodium bisulphite form piperidine sulphonic acids (B. **28**, 1459, 2273).

3. Nitric acid oxidizes piperidyl urethane (5) to γ-carbethoxyl-amidobutyric acid (6), which yields γ-amidobutyric acid or piperidic acid with caustic potash.

4. Potassium permanganate oxidizes benzoyl piperidine (7) to δ-benzoyl-amido-n-valeric acid (8), which is changed by caustic potash to δ-amido n-valeric acid (9) or homopiperidic acid (B. **17**, 2544).

5. Piperidine and methyl iodide form dimethylpiperidinium iodide (10), which moist silver oxide converts into dimethylpiperidinium hydroxide (11). This breaks down, on distillation, into dimethylpiperidine, the Δ_4-pentenyldimethylamine (12) and water. If Δ_4-pentenyldimethylamine be converted into Δ_4-pentenyltrimethylammonium hydroxide (13), and the latter be distilled, it will break down into piperylene (1, 99) or [1,4-pentadiën] (14), trimethylamine, and water (A. W. Hofmann, Ladenburg, B. **16**, 2058; compare the decomposition of the pyrrolidines, p. 461). The diagram affords a review of the preceding decomposition-reactions:



Piperidine, being an imide base, is capable of forming a nitroso-compound, n-alkyl- and n-acid-derivatives:

Nitrosopiperidine, $C_5H_{10}N.NO$, boiling at 218°, results from the action of nitrous acid upon piperidine. By reduction it becomes **Piperylhydrazine**, $C_5H_{10}N.NH_2$, boiling at 146°. See B. **30**, 535, for the electrolytic reduction of nitrosopiperidine and the formation of dipiperidyl. n-**Methyl Piperidine**, $C_5H_{10}N.CH_3$, boils at 107°. n-**Ethyl Piperidine** boils at 128°. n,γ-**Brompropylpiperidine** and **trimethylene piperylium bromide**, $C_5H_{10}:NBr<\genfrac{}{}{0pt}{}{CH_2}{CH_2}>CH_2$. See B. **29**, 2389.

The great reactivity of piperidine with brom- and iod-benzenes, resulting in the production of n-phenylpiperidine (B. **21**, 1021), is very peculiar. This power is very materially reduced in the case of α-methyl piperidine (B. **23**, 1388).

n-**Phenyl Piperidine**, $C_5H_{10}NC_6H_5$, boils at 250°. n-α- and β-**Naphthyl Piperidine**, boiling at 215° and melting at 50°, are obtained without difficulty from the naphthols and piperidine (B. **29**, 1175).

n-**Acetyl Piperidine**, $C_5H_{10}NCOCH_3$, boils at 226°. n-**Benzoyl Piperidine**, $C_5H_{10}NCOC_6H_5$, melting at 48°, condenses when heated with benzaldehyde to dibenzylpyridine (p. 532). **Piperidyl Urethane**, $C_5H_{10}NCO_2C_2H_5$, boils at 211°. The oxidation of benzoyl piperidine and piperyl urethane leads to the rupture of the piperidine nucleus. See p. 539. *Piperine, the alkaloid, is the piperide of piperic acid.*

The *homologous piperidines* result when the homologous pyridines are reduced with sodium and alcohol. They are called **pipecolines**, $C_5H_9(CH_3)NH$, **lupetidines**, $C_5H_8(CH_3)_2NH$, **copellidines**, $C_5H_8(CH_3)(C_2H_5)NH$, etc. (compare B. **28**, 2270.)

The alkyl piperidines contain asymmetric carbon atoms, hence different members of this class of bases have been decomposed, by means of their bitartrates, into optically active components—*e. g.*, α-**pipecoline** (B. **29**, 43, 422), the **copellidine**, boiling at 163° (B. **29**, 1959), obtained from aldehyde collidine, and β-**propyl piperidine**, boiling at 174° (B. **30**, 1060), isomeric with conine, which has been synthetically prepared from ε-chlor-β-propylamylamine.

α,α₁-**Diphenyl Piperidine** melts at 69° (B. **30**, 1499).

n-**Methyl-α-pipecolyl Alkine**, $C_5H_9[CH(OH)CH_3]NCH_3$, boils at 215°, and n-**Methyl-α-vinyl piperidine**, $C_5H_9(C_2H_3)NCH_3$, boils at 162° (C. 1897, I, 386).

***Triacetonamine** and **vinyl diacetonamine** (I, 219) are keto-derivatives of the piperidine series:*

$$CO<\genfrac{}{}{0pt}{}{CH_2-C(CH_3)_2}{CH_2-C(CH_3)_2}>NH \qquad CO<\genfrac{}{}{0pt}{}{CH_2-CH(CH_3)}{CH_2-CH(CH_3)_2}>NH.$$

They are produced in the action of diacetonamine upon acetone and benzaldehyde. The *oxime* of the vinyldiacetonamine, melting at 151°, yields upon reduction, depending upon the prevailing conditions, two stereoisomeric

γ-**Amidotrimethyl piperidines**, $NH_2CH<\genfrac{}{}{0pt}{}{CH_2-CH(CH_3)}{CH_2-C(CH_3)_2}>NH$ (*α-body* melting at 26° and boiling at 84–86° (20 mm.); the *β-body*, an oil, boiling at 82–84° [22 mm.]), which nitrous acid changes to two stereoisomeric **vinyldiacetonalkamines**, or γ-**oxytrimethyl piperidines**, $C_5H_7N(OH)(CH_3)_3$, melting at 138° and 161°. The latter is rearranged by sodium amylate into the first (A. **294**, 336).

Sodium and alcohols reduce the pyridine carboxylic acids to *piperidine carboxylic acids:*

Pipecolinic Acid, $C_5H_{10}N(COOH)$, melting at 261°, is resolved by the bitartrates into d- and l-pipecolinic acids, melting at 270° (B. **29**, 2887). **Hexahydroquinolinic Acid**, $C_5H_9N(COOH)$, has been obtained, similar to the hydrophthalic acids, in two stereo-isomeric forms, melting at 227° and 253°, of which each in the form of its *nitroso*-compound can be decomposed into two optically active forms (consult B. **29**, 2665). **Hexahydrocinchomeronic acid** melts with decomposition at 256° (B. **29**, 2187). **Eucaïne**, *derived from triacetonamine, is an oxycarboxylic acid derivative of the piperidine series.* It is a **tetramethyl-n-methyl-γ-benzoxypiperidine-γ-carboxylic ester**, $(CH_3)N<\genfrac{}{}{0pt}{}{C(CH_3)_2-CH_2}{C(CH_3)_2-CH_2}>C<\genfrac{}{}{0pt}{}{OCOC_6H_5}{COOCH_3}$, which has been recommended as a substitute for cocaïne as an anæsthetic (C. 1896, II, 709).

Conine, or α-propyl piperidine, *tropine*, and *ecgonine* are other important piperidine compounds. They are alkaloids or decomposition products of the latter. They will be discussed later, in the chapter relating to alkaloids.

Condensed nuclei, obtained from pyridine, have been prepared in great numbers, and are arranged in the following groups: II. *Quinolines*. III. *Condensed Quinolines—e. g.*, naphthoquinolines, anthraquinolines, phenanthrolines, quinoquinolines. IV. *Isoquinolines*. V. *Phenanthridines*. VI. *Naphthyridines* and *Naphthinolines*. VII. *Acridines* (carbazacridines, quinacridines). VIII. *Anthrapyridines*. The alkaloids attach themselves as a distinct chapter to the preceding bodies.

II. QUINOLINE GROUP.

The quinoline bases, or benzopyridine group, occur with those of pyridine in bone oil (coal-tar), and are obtained by distilling different alkaloids with lime. The parent substance of the group was first obtained by Gerhardt (1842) from the alkaloids quinine and cinchonine.

As regards synthetic methods, transpositions, and isomerides, quinoline is a naphthalene in which an α-CH-group is replaced by N.

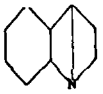
This was first shown by synthesizing quinoline from allyl aniline. This is perfectly analogous to the synthesis of naphthalene from phenyl butylene (p. 390) (Königs):

$$\underset{\text{Allyl Aniline}}{C_6H_5.NH.CH_2.CH:CH_2} = \underset{\text{Quinoline.}}{C_6H_4\left\langle\begin{matrix} N - CH \\ \quad\;\; | \\ CH = CH \end{matrix}\right.}$$

A more direct proof of the constitution of quinoline was effected through its formation from hydrocarbostyril (p. 391); PCl_5 converts the latter into a dichloride, which upon heating with hydriodic acid yields quinoline (A. Baeyer, B. 12, 1320):

$$\underset{\text{Hydrocarbostyril}}{C_6H_4\left\langle\begin{matrix} CH_2.CH_2 \\ NH \text{------} \end{matrix}\right\rangle CO} \longrightarrow \underset{\alpha\beta\text{-Dichlor-quinoline}}{C_6H_4\left\langle\begin{matrix} CH:CCl \\ N \text{------} \end{matrix}\right\rangle CCl} \longrightarrow \underset{\text{Quinoline.}}{C_6H_4\left\langle\begin{matrix} CH:CH \\ N \text{------} \end{matrix}\right\rangle CH}$$

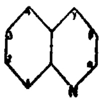
A "diagonal formula" has been suggested for quinoline because of its production in the distillation of acridine:



Owing to the intimate genetic relations prevailing between the quinoline and pyridine derivatives we must assume for the pyridine nucleus of quinoline the same linkages as in pyridine itself (see p. 526). Furthermore, later researches upon the formation of quinoquinolines (p. 553) from quinolines afford additional proof against the "diagonal formula" (A. 273, 1).

Isomerisms of the Quinoline Derivatives:

We represent the three replaceable hydrogen atoms of the pyridine nucleus in quinoline by α, β, and γ; those of the benzene nucleus with 1, 2, 3, and 4.



The positions 1, 2, 3, referred to the N-atom, correspond to the ortho-, meta-, and para-positions of the benzene derivatives; 4 is known as the *Ana*-position. These positions are designated as the affinities of the benzene nucleus with o-, m-, p-, and *a*. Another nomenclature designates the affinities of the pyridine nucleus as Py-1, -2, and -3; those of the benzene nucleus as B-1, -2, -3, and -4. Consequently, seven mono-derivatives of quinoline are possible (B. **19**, R. 443).

Syntheses of the Quinoline Derivatives:

1. The condensation of the ortho-amido-compounds of such benzene derivatives as have an oxygen atom attached to the third carbon atom of the side-chain.

In this way we obtain quinoline from o-*amido-cinnamic aldehyde*, $C_6H_4{<}^{NH_2}_{CH:CH.COH}$, *a*-methyl-quinoline from o-*amido-cinnamic methyl ketone*, and *a*-oxy-quinoline (carbostyril) from o-amido-cinnamic acid.

2. The condensation of o-amidobenzaldehyde or o-amidobenzoketones with substances containing the group $—CH_2—CO—$ (*e. g.*, aldehydes, ketones, acetoacetic ester, malonic ester) to quinolines by means of sodium hydroxide is dependent upon the intermediate formation of such o amido-derivatives (Friedländer, B. **16**, 1833; **25**, 1752):

$$C_6H_4{<}^{CHO}_{NH_2} + \begin{matrix}CH_3\\ |\\ CO.CH_3\end{matrix} \longrightarrow C_6H_4{<}^{CH=CH}_{N=CCH_3}$$

o-Amidobenzaldehyde Acetone *a*-Methyl Quinoline.

γ-Oxyquinolines are similarly formed from anthranilic acid (p. 211) with aldehydes, ketones, etc. (Ch. Zt. **17**, Rep. 258; see also B. **28**, 2809).

The synthesis of quinoline from o-toluidine and glyoxal and that of β-oxyquinaldine from o-toluidine and pyroracemic ester are similar (B. **27**, 628; **28**, R. 743):

$$C_6H_4{<}^{CH_3}_{NH_2} + \begin{matrix}OCH\\ |\\ OCH\end{matrix} \longrightarrow C_6H_4{<}^{CH=CH}_{N=CH}.$$

3. The production of quinoline and its derivatives substituted in the benzene nucleus by heating anilines with glycerol and sulphuric acid to about 140°, with the addition of nitrobenzene, or, better, arsenic acid (B. **29**, 703) as the oxidizing agent. This method is of universal application, and can be very readily executed (Skraup):

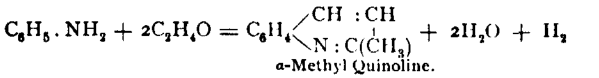
$$\underset{\text{Aniline}}{C_6H_5.NH_2} + \underset{\text{Glycerol}}{C_3H_8O_3} = \underset{\text{Quinoline.}}{C_6H_4N(C_3H_3)} + 3H_2O + H_2.$$

It is very probable that acroleïn first results, this then combines with the aniline derivative yielding acroleïn-aniline, which is oxidized to the quinoline derivative by the elimination of two hydrogen atoms by sulphuric acid. The halogen, nitro-, oxyanilines, toluidines, etc., behave similarly. The naphthylamines yield the naphthoquinolines; and the diamidobenzenes, the phenanthrolines.

Instead of using a mixture of the aromatic aniline and nitrobenzene, the corresponding nitro-body alone can be employed, which then is reduced in part by the hydrogen arising in the reaction. The first synthesis of this description was the preparation of alizarin blue (p. 554) from nitroalizarin (p. 427), glycerol, and sulphuric acid (A. **201**, 333).

The following may be regarded as further generalizations of these syntheses:

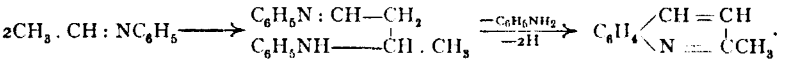
4 (a). Quinolines substituted both in the benzene and pyridine nucleus are produced in the condensation of anilines with aldehydes, aided by sulphuric or hydrochloric acid (*Quinaldine syntheses* of Doebner and v. Miller). Aniline and acetaldehyde yield α-methyl quinoline or quinaldine:



α-Methyl Quinoline.

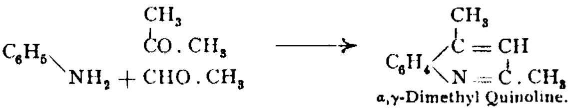
All aldehydes of the formula CHO . CH_2R react like acetaldehyde. The first step in the reaction consists in two molecules combining to unsaturated aldehydes, CHO . CR : CH . CH_2R, or condensing to aldols corresponding to them. These then act upon the anilines and form quinoline bases with a CH_2-group in the α-position.

It is very probable that alkylidene anilines formed at first change to dimolecular, aldol-like condensation-products, which split off aniline and become quinaldines (B. **25**, 2864; **29**, 59; compare formation 2 of the indols, p. 466):



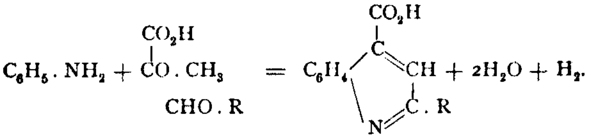
The hydrogen set free sometimes occasions a partial reduction of the reaction-product to tetrahydroquinoline derivatives (p. 550).

(b) Instead of two molecules of the same aldehyde, a mixture of two aldehydes, or an aldehyde with a ketone, may be used; in the latter case α,γ-di- or α,β,γ-trialkyl quinolines are formed (C. Beyer, B. **20**, 1908)—*e. g.*:



α,γ-Dimethyl Quinoline.

(c) *α-Alkylcinchoninic acids* (α-alkyl-quinoline-γ-carboxylic acids) are produced by the interaction of a mixture of pyroracemic acid and an aldehyde upon aniline (p. 549) (B. **281**, I):



This is a reaction which, particularly when naphthylamine is substituted for aniline, proceeds so smoothly that the production of naphtho-cinchoninic acids may be applied as a test for the *detection of aldehydes in mixtures*. Pyroracemic acid alone, when heated with aniline, yields the α-methyl quinoline-γ-carboxylic acid (aniluvitonic acid), together with phenyl lutidone; this is because aldehyde is formed from one molecule of the pyroracemic acid.

5. Oxyquinoline derivatives are obtained from aniline derivatives of β-ketonic acids and β-dicarboxylic acids by a ring formation (L. Knorr, B. **17**, R. 147; A. **236**, 112).

(a) Acetoacetic anilide (from aniline and acetoacetic ester when heated to 110°), when acted upon with concentrated acids, forms α-oxy-γ-methyl quinoline (γ-methyl carbostyril (Knorr, A. **236**, 112):

$$\begin{array}{l}OC(CH_3)CH_2\\ \qquad\quad |\\ C_6H_5(NH).CO\end{array} = C_6H_4\left\langle\begin{array}{l}C(CH_3):CH\\ \qquad\qquad |\\ N\cdots\cdots C(OH)\end{array}\right. + H_2O$$

Acetoacetic Anilide — γ-Methyl-α-oxyquinoline.

Methyl acetoacetic anilide by the same treatment yields β,γ-dimethyl carbostyril and acetoacetic methyl anilide gives the methyl derivative of γ-methyl pseudocarbostyril.

(b) On the other hand, β-anilido-crotonic ester, formed at the ordinary temperatures, yields *γ-oxy-α-methyl* quinoline when heated to 240° (Conrad and Limpach, B. **24**, 2990):

$$\begin{array}{l}RO.CO.CH\\ \qquad\qquad \|\\ C_6H_5.NH.C.CH_3\end{array} \longrightarrow C_6H_4\left\langle\begin{array}{l}C(OH):CH\\ \qquad\qquad |\\ N\cdots\cdots C.CH_3\end{array}\right.$$

β-Anilido-crotonic Ester — α-Methyl-γ-oxyquinoline.

Benzoyl acetic ester, acetone dicarboxylic ester, etc., react similarly. Benzanilide-imide chloride (p. 199) and sodium malonic ester yield anilbenzoylmalonic ester, which condenses to α-phenyl-γ-oxyquinoline-β-carboxylic ester (B. **19**, 1541):

$$C_6H_5\left\langle\begin{array}{l}\qquad RO.CO.CH.CO_2R\\ \qquad\qquad\qquad |\\ N\cdots\cdots\cdots\cdots CC_6H_5\end{array}\right. \longrightarrow C_6H_4\left\langle\begin{array}{l}C(OH)=C.CO_2R\\ \qquad\qquad\quad |\\ N\cdots\cdots C.C_6H_5\end{array}\right.$$

Anilbenzoyl Malonic Ester — α-Phenyl-γ-oxyquinoline-β-carboxylic Ester.

Phosphorus pentachloride converts malonanilidic acid into *α,β,γ-trichlorquinoline* (B. **18**, 2975; **20**, 1235); the alkyl malonic acids react similarly.

6. The conversion of *indols* and alkyl indols into trialkylic *dihydroquinolines*, analogous to that of pyrrols into pyridines by alkyl iodides, has been described upon p. 467. β-Brom- and chlorquinaldines are produced on heating methyl ketol with sodium alcoholate and CCl_3H or CBr_3H (B. **21**, 1940).

Behavior: The quinoline bases are liquids which dissolve with difficulty in water, readily in alcohol and ether, and possess a penetrating odor. Like the pyridines, they are tertiary bases, and like them form:

1. *Salts* and *double salts* (see mercury salts, B. **28**, R. 617). The platinum double salts are not changed by boiling (p. 530).

2. Ammonium-(*quinolinium*-)compounds are formed by their union with alkyl iodides. The additive power for alkyl iodides is, however, limited by the character of the substituents present in the quinolines (B. **24**, 1984).

The hydroxides obtained from the alkyl quinolinium iodides are unstable, just like the pyridinium hydroxides. They are so altered by sodium hydroxide that dihydroquinolines and α-oxodihydroquinolines (α-quinolons) are formed side by side (A. **282**, 363):

$$2C_6H_4\left\langle\begin{array}{l}CH=CH\\ N=CH\\ \wedge\\ CH_3\ OH\end{array}\right. \begin{array}{l}\longrightarrow C_6H_4\left\langle\begin{array}{l}CH=CH\\ N(CH_3)-CH_2\end{array}\right.\\ \longrightarrow C_6H_4\left\langle\begin{array}{l}CH=CH\\ N(CH_3)-CO\end{array}\right.\end{array}$$

Magnificent blue dyes, the *Cyanines*, which, however, are unstable, and the constitution of which is not definitely known, are obtained by treating mixtures of alkyl quinolinium iodides and homologous alkyl quinolinium iodides with caustic potash (B. **18**, R. 171).

When the quinolinium hydroxides are treated with alcohols, water splits off, and *alcoholates* $\left(-\overset{\|}{N}<^{OR}_{CH_3}\right)$ remain.

3. Quinoline, like pyridine, is but slightly attacked by nitric acid or chromic acid. Potassium permanganate, however, destroys the benzene nucleus in them, with production of *α,β-pyridine dicarboxylic acid* (quinolinic acid, p. 536).

The homologous quinolines, containing the alkyl groups in the pyridine nucleus, and those containing the substituents in the benzene nucleus are oxidized by chromic acid in the presence of sulphuric acid to the corresponding quinoline carboxylic acids, while potassium permanganate, on the other hand, usually oxidizes those substituted in the benzene nucleus, with the formation of *pyridine polycarboxylic acids* (B. **23**, 2252).

Potassium permanganate converts the α-alkyl quinolines, by the destruction of their pyridine nucleus, into acid derivatives of o-amidobenzoic acid. By this treatment α-phenyl quinoline yields *benzoyl anthranilic acid* (B. **19**, 1196).

The pyridine nucleus is similarly ruptured by the oxidation of the quinolinium compounds.

4. The pyridine nucleus of the quinolines, when reduced with zinc and hydrochloric acid, takes up four atoms of hydrogen, with the production of tetrahydroquinolines. Decahydroquinoline finally results by more energetic reduction.

The number of known quinoline derivatives is very great. To a certain extent they have a technical value as antiseptics, antipyretics, dyes, etc. Only the more important members of this group will receive consideration in the succeeding paragraphs.

Quinoline, C_9H_7N, is a colorless, strongly refracting liquid, with penetrating odor, which possesses a powerful antiseptic action. It boils at 239°; its sp. gr. = 1.095 at 20°. It occurs in bone-oil and coal-tar. It results when many alkaloids are distilled, and is best prepared synthetically by Skraup's method—*i. e.*, boiling a mixture of 38 grams aniline, 100 grams sulphuric acid, 24 grams nitrobenzene or arsenic acid, and 120 grams glycerol for several hours (B. **14**, 1002; **27**, 574; **29**, 704).

It forms crystalline and very soluble salts with one equivalent of acids; the characteristic bichromate, $(C_9H_7N_2)Cr_2O_7H_2$, dissolves with difficulty and forms yellow needles, melting at 165°.

Its *iodmethylate*, $C_9H_7N \cdot ICH_3$, melting at 72°, is converted by sodium hydroxide into n-methyldihydroquinoline and n-methyl-α-quinoline.

Quinoline betaïne, $C_9H_7N \cdot CH_2 \cdot CO \cdot O$ (N and O joined by a bond), melts at 171°. Its hydrochloride is formed from quinoline and chloracetic acid. *Di-*, *tetra-*, *hexa-*, and *decahydroquinoline* result from the reduction of quinoline (p. 551).

Homologous Quinolines.—The seven isomeric *methyl quinolines* are all known. The four quinolines, methylated in the benzene nucleus, sometimes called *toluquinolines* or *methylbenzquinolines*, are obtained by the reaction of Skraup from the three toluidines: o-methyl quinoline boils at 248°, the *para* at 257°, the *meta* at 248°, and the *ana* at 250°.

α-**Methyl-quinoline, Quinaldine,** $C_9H_6N(CH_3)$, boiling at 247°, occurs in coal-tar (25 per cent.) (B. **16**, 1082). It is produced by the various synthetic methods, by the reduction of *γ*-oxyquinaldine, and by fusing ethyl acetanilide, $C_6H_5N(C_2H_5) . CO . CH_3$, with zinc chloride (B. **23**, 1903). It may also be obtained by digesting aniline, paraldehyde, and crude hydrochloric acid for several hours (B. **16**, 2465).

Chromic acid oxidizes it to *α*-quinoline carboxylic acid (see p. 545).

The CH_3-group of quinaldine is very reactive. It enters readily into condensation products with aldehydes (paraffin or benzene class) (B. **20**, 2041). It combines with formaldehyde to *α-oxethyl quinoline*, which by loss of water forms *α-vinylquinoline*, $C_9H_6(C_2H_3)N$ (B. **27**, 2689). Chloral yields the compound, $C_9H_6N . CH : CH . CCl_3$, melting at 144°; boiling potassium carbonate converts it into *α*-**quinoline acrylic acid,** $C_9H_6N . CH : CH . CO_2H$, while potassium permanganate oxidizes it to *α*-**quinoline aldehyde,** $C_9H_6N . CHO$. Hydrobromic acid and soda convert quinoline acrylic acid into *α*-**quinoline-lactic acid** (B. **21**, R. 635; **28**, R. 752). Consult B. **22**, 271, upon quinoline acrylic acids and quinoline aldehydes. Quinaldine, oxalic ester, and sodium ethylate yield *quinaldine oxalic acid*, $(C_9H_6N)CH_2 . CO . COOH$ (B. **30**, 1479). Quinaldine and phthalic anhydride yield a beautiful yellow dye—**quinophthalone** or **quinoline yellow,** $C_6H_4(C_2O_2) : CH . N . C_9H_6$ (p. 240), melting at 235°. The sodium salt of its sulphonic acid is the **quinoline yellow** of commerce. It dyes silk and cotton a beautiful yellow.

See B. **29**, 187, for the action of quinaldine upon phthalaldehydic acids.

β-**Methyl Quinoline,** $C_9H_6(CH_3)N$ (B. **20**, 1916), boils at 250° and melts at 10–14°.

γ-**Methyl-quinoline, Lepidine,** occurs, together with quinoline and quinaldine, in coal-tar, and is obtained on distilling cinchonine with caustic potash. It may be synthetically prepared. It boils at 257°. Chromic acid oxidizes both methyl quinolines to the corresponding quinoline monocarboxylic acids. Potassium permanganate produces pyridine tricarboxylic acids.

α,β-**Dimethyl Quinoline,** $C_9H_5(CH_3)_2N$, boils at 261° (B. **22**, 267).

α,γ-**Dimethyl Quinoline,** boiling at 266°, is made from acetyl acetone and aniline, as well as from dihydrotrimethyl quinoline, which is produced by the interaction of indol and methyl iodide (p. 550).

β,γ-**Dimethyl Quinoline,** from *β,γ*-dimethyl carbostyril, melts at 65° and boils at 290°. o- and p-**Toluquinaldine,** $C_9H_5(CH_3)_2N$ (B. **23**, 3483).

α-**Ethyl Quinoline,** $C_9H_6(C_2H_5)N$, boils at 255–260°, *β*-**Ethyl Quinoline** at 265°. They result on heating ethyl quinolinium iodide to 250° (analogous to the formation of alkyl pyridines, p. 528). *γ*-**Ethyl Quinoline** boils at 270–275°.

Consult B. **21**, R. 138, upon the **trimethyl-quinolines.**

α-**Phenyl-quinoline,** $C_9H_6(C_6H_5)N$, is obtained from cinnamic aldehyde and aniline upon heating them with hydrochloric acid to 200°. It melts at 84° and boils above 300°. Potassium permanganate oxidizes it to benzoyl anthranilic acid. *β*-**Phenyl-quinoline** is an oil, which solidifies on cooling (B. **16**, 1836).

γ-**Phenyl-quinoline** is formed from its acid. It melts at 61°. It is closely related to the quinia alkaloids (B. **20**, 622). See B. **27**, 907 (p. 571), for *γ*-**Quinoline Phenols.**

Nitrophenyl Quinoline, $NO_2C_6H_4 . C_9H_6N$, melting at 159°, is formed from iso-diazonitrobenzene and quinoline (B. **29**, 168).

γ-**Phenyl-*α*-Methyl Quinoline,** *γ-phenyl quinaldine*, $C_9H_5(C_6H_5)(CH_3)N$, results by the condensation of benzoyl acetone with aniline (B. **20**, 1771). It melts at 99° and yields *γ*-phenyl quinoline-*α*-carboxylic acid when its phthalone is oxidized with chromic acid. This new acid affords *γ*-phenyl quinoline.

α-**Phenyl-*γ*-methyl Quinoline** is produced (B. **19**, 1036) by distilling flavenol with zinc-dust. It melts at 65°.

Its p-amido-derivative, **Flavaniline,** applied as a beautiful yellow dye (B. **15**, 1500), is *α*-**Amidophenyl-*γ*-methyl-quinoline,** $C_9H_5(CH_3)(C_6H_4NH_2)N$. It results in the condensation of o-amido-acetophenone and p-amido-acetophenone when digested with zinc chloride (B. **19**, 1038). Its monacid salts are yellow in color and have been used as dyes (B. **15**, 1500). Nitrous acid converts it into so-called **Flavenol,** $C_9H_5(C_6H_4 \cdot OH)(CH_3)N$, *α*,p-**Phenyl-*γ*-methyl-quinoline.**

Various isomeric **diquinolines**, $(C_9H_6N)_2$, have been prepared by boiling quinoline with sodium; further, by conducting its vapors through tubes heated to redness, and finally from benzidine and other diamidodiphenylenes through Skraup's quinoline synthesis (M. **8**, 121; B. **17**, 1965; **20**, 634, etc.).

Diquinolyl Quinoline, $C_9H_7N \cdot C_9H_6N \cdot C_9H_7N$, melting at 151°, is formed from γ-acetacetyl quinoline, $C_9H_7N \cdot COCH_2COCH_3$ (p. 549), with two molecules of o-amidobenzaldehyde (B. **29**, R. 845).

Triquinolyl Methane, $CH(C_9H_6N)_3$, melting at 202°, is obtained from pararosaniline by the reaction of Skraup (B. **24**, 1606, 2267). Consult p. 357 for the opinion that *aldehyde green* is a quinoline derivative.

Halogen, Sulpho-, and **Nitro-derivatives of the Quinolines.**—All those containing the substituents in the benzene nucleus are prepared by the methods in use for the introduction of such groups into benzene and naphthalene. Or the corresponding substituted benzene derivatives are subjected to the quinoline syntheses given on p. 544. It is more difficult to introduce the halogens, the nitro- or the sulpho-groups into the pyridine nucleus of quinoline. Py-chlorine derivatives of quinoline are chiefly made by the action of PCl_5 upon py-oxyquinolines. The ready mobility of the halogen atoms occupying the α- or γ-positions in quinoline is very remarkable. They can be easily replaced by OH, NHR, etc.

α-**Chlor-quinoline**, C_9H_6ClN, melting at 38° and boiling at 267°, is prepared from carbostyril and PCl_5 (B. **15**, 333). β-**Chlor-quinoline**, boiling at 255°, is produced from quinoline and sulphur chloride, along with the compound $(C_9H_5N)_2S_2$ and trichlorquinoline (B. **29**, 2456). α-**Brom-quinoline** melts at 49° (J. pr. Ch. [2], **41**, 41). α-**Brom-quinoline**, melting at 13° and boiling at 276°, results from the action of sulphur bromide upon quinoline or by heating quinoline hydrochloride with bromine (B. **27**, R. 732; **25**, R. 422; **29**, 2459). γ-**Chlor-quinoline**, melting at 34°, is obtained from kynurine and also from γ-amidoquinoline (B. **27**, R. 748). γ-**Brom-quinoline** results when PBr_5 acts upon kynurine (B. **27**, R. 732). α-**Iod-quinoline Iodmethylate**, $C_9H_6IN \cdot ICH_3$, melting at 212°, is produced when methyl iodide acts upon α-chlorquinoline (A. **282**, 376). α-**Methyl-β-chlor-quinoline**, melting at 72°, is produced from methyl ketol, CCl_3H and sodium alcoholate (B. **21**, 1942). α,β-**Dichlor-quinoline**, melting at 105°, results in the action of PCl_5 upon hydrocarbostyril. α,β,γ-**Trichlorquinoline**, $C_9H_4Cl_3N$, melting at 107°, is formed from malonanilic acid and PCl_5 (B. **17**, 737) (p. 544).

Amido-quinolines, substituted in benzene nucleus, are produced in the reduction of the corresponding nitroquinolines. The py-α- and γ-amido-quinolines result upon heating α- or γ-chlor- (brom-) quinolines with amines.

α-**Amido-quinoline**, $C_9H_6(NH_2)N$, melting at 114°, is produced by the reducing-decomposition of *α-phenylhydrazide-quinoline*, $C_9H_6(NH \cdot NHC_6H_5)N$, the reaction product of phenylhydrazine and α-chlorquinoline. The oxidation of phenylhydrazidoquinoline produces *α-phenylazoquinoline*, $C_9H_6(N : NC_6H_5)N$ (B. **24**, 2819).

α-**Amidoquinoline Iodmethylate**, $C_9H_6(NH_2)N \cdot ICH_3$, melting at 247°, is formed directly from ammonia and α-iod-quinoline iodmethylate (A. **282**, 380). α-**Phenylamido-quinoline**, $C_9H_6(NHC_6H_5)N$, melting at 98°, results upon heating α-chlorquinoline and aniline to 200° (B. **18**, 1532). γ-**Amido-quinoline**, melting at 142–144°, is formed when bromine and caustic potash act upon cinchoninamide (see amidopyridines, p. 533). γ-**Amido-quinaldine**, $C_9H_5(CH_3)(NH_2)N$, melts at 270° (B. **21**, 1980). p-**Methoxy-γ-amidoquinoline**, $C_9H_5(OCH_3)(NH_2)N$, melting at 120°, results when potassium hypobromite acts upon the amide of quinic acid (B. **29**, R. 674).

Oxyquinolines.—The oxyquinolines manifest the character both of bases and of phenols. Those containing the hydroxyl in the benzene nucleus, called also quinophenols or oxybenzquinolines, are synthesized from the three amidophenols by Skraup's and Döbner-Miller's reactions; also by reduction of the Bz-nitroquinolines, or from the quinoline sulphonic acids by fusion with caustic potash (B. **28**, R. 912).

1-**Oxyquinoline**, $C_6H_3(OH) : (C_3H_3N)$, is most readily prepared from 1-quinoline sulphonic acid (B. **16**, 712). It melts at 75° and boils at 266°. From it is obtained **1-Ethoxy-4-acetamidoquinoline, analgen**, $C_6H_2(OC_2H_5)(NH \cdot COCH_3) : (C_3H_3N)$, melting at 155°, which has been recommended for the alleviation of pain. **p-Oxyquino-**

line, melting at 194°, results from the exit of carbon dioxide from xanthoquinic acid (p 550).

The Bz-oxyquinolines, when acted upon in glacial acetic acid solution (Zincke's method), are converted, like the naphthols, into chlorinated quinoline-quinones, which (similar to the conversion of naphthalene derivatives into indenes) are rearranged to **pyrindene**-derivatives of a condensed pyridine and indene ring. Thus, from p-oxyquinoline and chlorine by various transformations of the primary reaction-products, **dichlortriketotetrahydroquinoline** (1) results. This, on boiling with water, becomes **β-chlor-α-oxypyrindone** (2), from which **dichloracetopicolinic acid** (3) is obtained by rupture of the ring (A. 290, 321):

$$(1)\ C_5H_3N\begin{cases}CO-CO\\CO-CCl_2\end{cases} \longrightarrow (2)\ C_5H_3N\begin{cases}C(OH)\\CO\end{cases}\!\!\!>CCl \longrightarrow (3)\ C_5H_3N\begin{cases}COCHCl_2\\COOH\end{cases}.$$

The oxyquinolines, with hydroxyl in the pyridine nucleus, are more feeble bases and phenols than the oxybenzquinolines. As in the case of the oxypyridines or pyridones (p. 534), it is undetermined whether the hydroxyl or keto-form should be given to the oxyquinolines of the α- and γ-positions. Ethers, however, of the two forms—*e. g.*, *carbostyril* and *pseudocarbostyril*—exist:

$$C_6H_4\begin{cases}CH:CH\\N:C.OR\end{cases} \text{ and } C_6H_4\begin{cases}CH:CH\\NR.CO\end{cases};\quad C_6H_4\begin{cases}C(OR):CH\\N{=\!=}CH\end{cases} \text{ and } C_6H_4\begin{cases}CO-CH\\NR-CH\end{cases}$$

α-Oxyquinoline, Carbostyril, $C_9H_7ON(+H_2O)$, the lactime or lactam of o-amido-cinnamic acid (p. 214), is most readily obtained by the reduction of o-nitro-cinnamic ester (B. 14, 1916). It may also be prepared from α-chlorquinoline by heating it with water, and by digesting quinoline with a bleaching lime solution (B. 21, 619). It melts at 199°.

Water decomposes its salts with alkalies and acids. Potassium permanganate oxidizes it to oxalyl anthranilic acid, $C_6H_4<^{COOH}_{NH.CO.CO_2H}$. Sodium and alcohol reduce it to tetrahydroquinoline.

Carbostyril Methyl Ether, boiling at 247°, and the *ethyl ether*, boiling at 256°, or α-methoxy- and *ethoxy-quinolines*, are oils. They are produced by the action of the alkyl iodides upon the Na- or Ag-salts of carbostyril, by the action of sodium alcoholates upon α-chlorquinolines, and when o-amidocinnamic esters are digested with alcoholic zinc chloride.

The *pseudocarbostyril ethers*—the *methyl*, melting at 71°; and the *ethyl*, at 54°—are produced by the action of the alkyl iodides upon free carbostyril in the presence of alkalies. Also when sodium hydroxide acts upon methyl- and ethyl-quinolinium iodide (p. 544). n-Methyl quinolon is also produced when ethoxyquinoline is heated with methyl iodide (B. 30, 930).

1-Nitrocarbostyril, $C_9H_6(NO_2)ON$, melting at 168°, results from the action of alcoholic ammonia upon nitrocoumarin. **3-Oxycarbostyril,** melting beyond 300°, is formed by the condensation of 6-amido-m-coumaric acid, which is produced in the electrolytic reduction of o-nitrocinnamic acid.

γ-Methyl-α-oxyquinoline, γ-Methyl Carbostyril, or **Lepidone,** $C_9H_6(CH_3)ON$, melting at 223° and boiling at 270° (17 mm.), is obtained from acetoacetanilide (p. 544). Its lactime ether, *α-Methoxy-γ-methyl quinoline*, boiling at 276°, results when $NaOCH_3$ acts upon α-chlorlepidine. The lactam ether: n-*methyl lepidone*, melting at 131°, is prepared from acetoacetic ester and methyl aniline (p. 543), and by heating ethoxylepidine with methyl iodide (B. 30, 931).

β-Oxy-α-methyl Quinoline, *γ-Oxyquinaldine*, $C_9H_6(CH_3)ON(+2H_2O)$, melting at 231°, from β-anilido-crotonic ester (p. 543), also forms two isomeric ethers:

γ-Methoxyquinaldine, boiling at 298°, and n-*methyl quinaldone*, melting at 175° (B. 22, 78). With methyl iodide both ethers yield the same *iodmethylate*,

$$C_6H_4<\begin{matrix}C(OCH_3) = CH \\ N(ICH_3) = \overset{|}{C} . CH_3\end{matrix}$$, which upon heating or treatment with alkalies becomes n-methyl quinaldone (B. 30, 922). Compare the similar behavior of methoxyphenylmethyl pyrazole and antipyrine.

γ-**Oxyquinoline, Kynurine,** $C_9H_6(OH)N$, is made by heating kynurenic acid (oxyquinoline carboxylic acid), and by oxidizing cinchonine and cinchoninic acid with chromic acid (B. 22, R. 758). It melts at 201°. PCl_5 converts it into γ-chlorquinoline (B. 27, R. 748) (p. 547).

p,γ-**Dioxyquinoline,** $C_9H_7O_2N$, results in the saponification of p-methoxykynurine, which is formed when nitrous acid acts upon p-methoxy-γ-amidoquinoline (B. 29, R. 675).

α,γ-**Dioxyquinoline,** $C_9H_7O_2N$, sublimes. It is formed when caustic potash acts upon γ-bromcarbostyril and upon digesting α-amidophenyl propiolic acid with SO_4H_2 (B. 15, 2151) (p. 284). The reduction of its β-nitroso derivative produces α,β,γ-**trioxyquinoline,** $C_9H_7O_3N$, which ferric chloride oxidizes to quinisatinic acid (p. 261) and **quinisatin** or **triketotetrahydroquinoline** (B. 17, 985).

Quinoline Aldehydes and **Quinoline Ketones** :

α-**Quinoline Aldehyde,** $C_9H_6(CHO)N$, melting at 71°, is obtained from quinoline acrylic acid (p. 546) with potassium permanganate.

Py-Quinoline ketones are produced by synthetic method 2 (p. 542) from o-amidobenzaldehyde and β-diketones :

β-**Acetyl Quinaldine,** $C_9H_5(CH_3)(COCH_3)N$, melts at 57.5° (B. 25, 1756.)

β-**Acetyl Carbostyril,** $C_9H_6(COCH_3)ON$, melting at 232°, is formed from o-amidobenzaldehyde and acetoacetic ester (B. 16, 1838).

γ-**Acetacetyl Quinoline,** $C_9H_7N(CO . CH_2 . CO . CH_3)$, melting at 65° and boiling at 206° (17 mm.), is prepared from cinchoninic ester, acetone, and sodium ethylate. It condenses with phenylhydrazine to *phenylquinolylmethyl pyrazole*, melting at 120°, and with two molecules of o-amidobenzaldehyde to *diquinolyl quinoline* (p. 547 ; B. 29, R. 845).

Quinoline Carboxylic Acids: They exhibit the character of amido-acids. Those substituted in the benzene nucleus have been synthesized from the amido benzoic acids (B. 28, 2809), and are produced when Bz-alkyl quinolines are treated with chromic acid. The Py-quinoline carboxylic acids also result from the action of a chromic acid mixture upon Py-alkyl quinolines. The alkyl groups in the γ-position are most easily oxidized ; the β- with more difficulty, and the alkyl groups in the α-position with the greatest difficulty (B. 23, 2254) (p. 544). When they are heated, carbon dioxide is expelled and the respective quinolines are produced. The acids, carrying the carboxyl in the α-position, are colored reddish-yellow by ferrous sulphate.

o-**Quinoline Carboxylic Acid,** $C_9H_6N(COOH)$, melts at 187°. The *meta*-acid melts at 248-250°. The *para*-acid melts at about 291°. The *ana*-acid melts at 360° (A. 237, 325 ; B. 19, R. 443, 548).

α-**Quinoline Carboxylic Acid, Quinaldic Acid,** crystallizes from hot water in needles containing $2H_2O$; it melts at 156°, and decomposes. It is obtained from quinaldine.

β-**Quinoline Carboxylic Acid** is also produced by heating *Acridic Acid.* It melts at 171°.

γ-**Quinoline Carboxylic Acid, Cinchoninic Acid,** was first produced upon oxidizing cinchonine with potassium permanganate or nitric acid. It contains 1 or $2H_2O$ (B. 20, 1609). It melts at 254°. It readily affords quinoline ; potassium permanganate oxidizes it to α,β,γ-pyridine tricarboxylic acid.

α-Alkyl Cinchoninic Acids result from the condensation of aldehydes with pyroracemic acid and anilines (B. 22, R. 23 ; A. 281, 1) (p. 543).

α-**Methyl Cinchoninic Acid, Aniluvitonic Acid,** $C_9H_5(CH_3)(COOH)N(+H_2O)$, is obtained by the condensation of pyroracemic acid with aniline (p. 84) (B. 22, 1769). It melts at 240°, and breaks down.

α-**Methyl-quinoline-β-carboxylic Acid** results from the condensation of o-amidobenzaldehyde with acetoacetic ester (p. 543), and melts at 234° with decomposition.

Acridic Acid, α,β-Quinoline-dicarboxylic Acid, $C_9H_5N(COOH)_2$, is produced when acridine is oxidized with potassium permanganate, just as quinoline yields α,β-pyridine dicarboxylic acid. It crystallizes in needles with $2H_2O$, or plates with $1H_2O$, and decomposes at 120–130°.

α,γ-Quinoline-dicarboxylic Acid results when α-cinnamenyl-cinchoninic acid is oxidized with potassium permanganate (B. **22**, 3009). It melts at 246° with decomposition.

Oxyquinoline Carboxylic Acids:

α-Oxyquinoline-β-carboxylic Acid, $C_9H_5(OH)(COOH)N$, results in the condensation of o-amido benzaldehyde with malonic acid (p. 543) and melts above 320°.

α-Oxyquinoline-γ-carboxylic Acid is formed on melting cinchoninic acid with potash. It melts at 310° and decomposes. Both acids decompose into CO_2 and carbostyril on heating their silver salts.

Kynurenic Acid is a *γ-oxyquinoline carboxylic acid.* It occurs in the urine of dogs after the ingestion of meat. It contains $1H_2O$ and melts at 257°. Fusion with caustic potash converts it into CO_2 and kynurine.

p-Oxyquinoline-γ-carboxylic Acid, $C_9H_5(OH)N(CO_2H)(+H_2O)$, *Xanthoquinic acid*, results on fusing parasulphocinchoninic acid with KOH. It melts at 320° with decomposition. Its *methylphenol ether*, **Quinic Acid,** $C_9H_5(O.CH_3)N(CO_2H)$, is obtained by oxidizing quinine and quinidine with chromic acid in sulphuric acid solution. It melts at 280°.

γ-Oxyquinaldine-β-carboxylic Acid, $C_9H_4(CH_3)ON(COOH)$, melting at 245° with decomposition, results in the condensation of anthranilic acid with acetoacetic ester (B. **27**, 1396).

HYDROQUINOLINES.

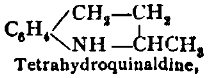
Dihydroquinolines are obtained on treating alkyl quinolinium iodides with sodium hydroxide. Thus, the iodmethylate of cinchoninic acid yields n-*methyl dihydrocinchoninic acid*, $C_6H_4:[C_3H_5(COOH)N.CH_3]$, along with n-*methyl quinolon-γ-carboxylic acid* (A. **282**, 365; compare B. **25**, 3326). These substances are, however, very easily altered.

Methyl iodide and trimethyl indol (p. 468) yield a base having the formula of a *trimethyldihydroquinoline*, $C_9H_6N(CH_3)_3$, boiling at 244°, which, however, upon the distillation of its iodmethylate again affords trimethyl indol, and by oxidation trimethyl indolinone (p. 471). It is reduced to a base having the formula of a *trimethyltetrahydroquinoline*, $C_9H_8N(CH_3)_3$, which is also convertible into a dimethyl quinoline, but in other respects exhibits a behavior different from that of other tetrahydroquinolines (B. **29**, 2460).

Ketodihydroquinolines or *quinolons* are the n-alkyl ethers of the oxyquinolines (p. 548).

Tetrahydroquinolines: These are produced when the quinolines are reduced with tin and hydrochloric acid, or with sodium and alcohol. The pyridine nucleus then takes up four hydrogen atoms. This procedure changes the chemical nature of the quinolines very materially. *The tetrahydroquinolines behave like secondary fatty-aromatic amines.* Nitrous acid converts them into n-nitrosamines, which readily rearrange themselves to Bz.p-nitrosamines. With the salts of diazobenzene they yield diazoamido-compounds, which readily pass over into p-azophenyl derivatives. This alteration in the chemical character of quinoline is similar to that seen in the indols by their change to dihydroïndols (p. 471). The tetrahydroquinolines are to be regarded as ring-homologues of the dihydroïndols:

Dihydromethyl Ketol



Tetrahydroquinaldine.

whereas the basal substances, the indols and the quinolines, behave very differently. The tetrahydroquinolines are oxidized to quinolines again by chromic acid, silver acetate, or $Hg(NO_3)_2$ (B. **27**, 824).

Tetrahydroquinoline, $C_9H_{11}N$, boiling at 244°, is liquid at the ordinary temperature. It is formed when tin and hydrochloric acid act upon quinoline and α- and γ-chlorquinolines; also by the action of sodium and alcohol upon carbostyril (B. **23**, 1142). Nitrous acid converts it into a *nitroso*-body, which is easily rearranged to p-*nitrosotetrahydroquinoline*, melting at 134° (B. **16**, 732). With benzoyl chloride it forms n-*benzoyltetrahydroquinoline*, melting at 75°; with methyl iodide, n-**Methyl tetrahydroquinoline, kairoline,** $C_9H_{10}N.CH_3$, boiling at 245°, which is said to have the same action as **kairine** (a febrifuge), the hydrochloride of o-oxy n-**methyltetrahydroquinoline,** $C_9H_9(OH)N.CH_3$, melting at 114°, and **thallin,** the sulphate of p-**methoxytetrahydroquinoline,** $C_9H_9(OCH_3)NH$, melting at 42° and boiling at 283°, and possessing the action of a febrifuge.

Tetrahydrotoluquinoline, $CH_3.C_6H_3:[C_3H_7N]$, boiling at 257°, is produced on boiling toluidine with trimethylene chlorobromide (B. **24**, 2061; **25**, 2805):

$$CH_3.C_6H_4NH_2 + \begin{array}{l}BrCH_2.CH_2\\ \quad | \\ ClCH_2\end{array} \longrightarrow CH_3.C_6H_3\begin{array}{l}/CH_2-CH_2\\ \quad\quad\quad\quad | \\ \backslash NH-CH_2\end{array}.$$

The *nitroso*-compound melts at 51°; the *benzene-diazo*-body at 99°.

Tetrahydroquinaldine, $C_6H_4\begin{array}{l}/CH_2-CH_2\\ \quad\quad\quad\quad | \\ \backslash NH-CH.CH_3\end{array}$, boiling at 247°, is also produced in the reduction of o-nitrophenethylmethyl ketone, $C_6H_4\begin{array}{l}/NO_2\\ \backslash CH_2.CH_2.COCH_3\end{array}$ (B. **14**, 890). It is changed to benzoylamido-phenylacrylic acid when its benzoyl derivative is oxidized. It has an asymmetric C-atom, and by means of its bitartrate it is resolved into two optically active components (B. **27**, 77). The δ-lactams of o-amidophenyl fatty acids—*e. g.*, **Hydrocarbostyril,** or o-amido-phenylpropionic acid lactam, are keto-derivatives of tetrahydroquinoline. Hydrocarbostyril has been obtained by the Beckmann rearrangement of α-hydrindone oxime (p. 387), as well as from its acid, β-**hydrocarbostyril carboxylic acid,** $C_9H_{10}NO(COOH)$, melting at 146° with decomposition. Its ester results in the reduction of nitrobenzyl malonic ester (B. **29**, 665). See pp. 253, 255, 256, for **oxyhydrocarbostyril. Quinisatine,** or o-amido-benzoyl glyoxylic acid lactam, is *triketotetrahydroquinoline.*

Hexa- and Decahydroquinolines: When quinoline or tetrahydroquinoline is heated to high temperatures with hydriodic acid and phosphorus, the benzene nucleus also takes up hydrogen, and the reaction-product yields, in addition to a little **hexahydroquinoline,** $C_9H_{13}N$, boiling at 226° (B. **27**, 1459), and other products:

Decahydroquinoline, $C_9H_{18}N$, melting at 48° and boiling at 204°. It is a very volatile, strongly alkaline substance, which has an odor astonishingly like that of conine. While tetrahydroquinoline resembles the mixed fatty aromatic bases, decahydroquinoline manifests the properties of a secondary amine of the aliphatic series. *It is the piperidine of the quinoline group:*

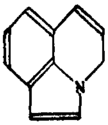
$$\begin{array}{c}CH_2-CH_2-CH_2\\ |\qquad\qquad\quad | \\ CH_2-NH-CH_2\\ \text{Piperidine}\end{array} \qquad \begin{array}{c}CH_2-CH_2-CH-CH_2-CH_2\\ |\qquad\qquad\quad |\qquad\qquad\quad | \\ CH_2-CH_2-CH-NH-CH_2\\ \text{Decahydroquinoline,}\end{array}$$

When its *benzoyl*- and *urethane*-derivatives are oxidized, decahydroquinoline sustains decompositions similar to those of piperidine; the products are benzoylated o-*amidohexahydrophenylpropionic acid* and the methyl urethane of o-*amidohexahydrophenylacetic acid:*

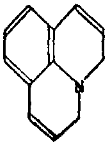
$$C_6H_{10}\begin{array}{l}/CH_2-\!\!-\!\!-CH_2\\ \quad\quad\quad\quad\quad\quad | \\ \backslash N(CO.C_6H_5).CH_2\end{array} \rightarrow C_6H_{10}\begin{array}{l}/CH_2-CH_2.COOH\\ \backslash NH(COC_6H_5)\end{array},\ C_6H_{10}\begin{array}{l}/CH_2-\!\!-\!\!-CH_2\\ \quad\quad\quad\quad\quad\quad | \\ \backslash N(CO_2CH_3).CH_2\end{array} \rightarrow C_6H_{10}\begin{array}{l}/CH_2.COOH\\ \backslash NH(CO_2CH_3)\end{array}$$

Free o-amidohexamethylenepropionic acid readily parts with water and becomes **Decahydrocarbostyril**, $C_6H_{10}<\begin{matrix}CH_2-CH_2\\ \quad\;\;\;\; | \\ NH-CO\end{matrix}$ (p. 300) (B. 27, 1458).

Julole and **lilole compounds** are derivatives of hydroquinolines. They are probably derived from the hypothetical parent substances:



Lilole



Julole.

Lilole must be considered as a combination of the quinoline nucleus with the pyrrol nucleus, or of the pyridine nucleus with the indol nucleus, while julole is a combination of the quinoline nucleus with the pyridine nucleus.

Diketomethyl Lilolidine, $\begin{matrix}CO-C_6H_3<\begin{matrix}CH_2\\ N\end{matrix}>CH\,.\,CH_3\\ | \qquad\qquad\quad | \\ CH_2 \text{———————} CO\end{matrix}$, is obtained from malonic ester and dihydromethyl ketol (p. 470). It has been described in connection with the latter.

Ketomethyl Juloline, $\begin{matrix}(CH_3)C-C_6H_3\diagup\begin{matrix}CH_2-CH_2\\ \qquad | \\ N\text{——}CH_2\end{matrix}\\ \| \qquad\qquad | \\ HC\text{———————}CO\end{matrix}$, melting at 130°, is formed from tetrahydroquinoline and acetoacetic ester (B. 24, 845).

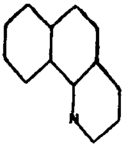
Julolidine, $\begin{matrix}CH_2-C_6H_3\diagup\begin{matrix}CH_2-CH_2\\ \qquad | \\ N\text{——}CH_2\end{matrix}\\ | \qquad\qquad | \\ CH_2\text{———————}CH_2\end{matrix}$, melting at 40°, is produced on boiling tetrahydroquinoline with one molecule of trimethylene chlorbromide, or aniline with two molecules of trimethylene chlorbromide (B. 25, 2801). Both julole derivatives are bases, whereas **diketojulolidine,** $\begin{matrix}CO-C_6H_3\diagup\begin{matrix}CH_2-CH_2\\ \qquad | \\ N\text{——}CH_2\end{matrix}\\ | \qquad\qquad | \\ CH_2\text{———————}CO\end{matrix}$, obtained from tetrahydroquinoline and malonic ester, has only acid properties.

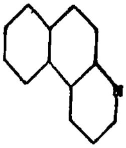
III. CONDENSED QUINOLINES.

Condensations similar to those effected through aniline in the quinoline syntheses can be carried out with the higher aromatic amines—*e. g.*, naphthylamine, anthramine, the amidoquinolines, the phenylenediamines, etc. All these amines yield with glycerol (Skraup), or with aldehydes, etc. (Döbner-Miller, p. 543), higher condensed bases, containing the quinoline nucleus.

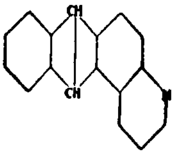
In these reactions the pyridine ring, as a rule, then attaches itself only to two such members of the benzene nucleus, which, according to the requirements of the Kekulé formula, are doubly linked (B. 26, R. 402; 27, R. 631). This would argue against the various centric and diagonal formulas which have been suggested for the derivatives of benzene and of pyridine.

A. *α*- and *β*-Naphthoquinolines are obtained from both naphthylamines:



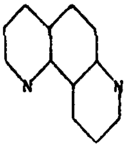


B. *Anthraquinolines* are formed from amidoanthracenes:

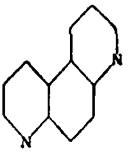


C. m- and p-Phenylenediamines yield *phenanthrolines* (I) and *pseudophenanthrolines* (II); a third isomeric *phenanthroline* (III) is obtained from o-amidoquinoline. For practical purposes these three isomerides may be distinguished as o-, m-, and p-phenanthrolines:

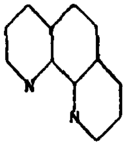
I.



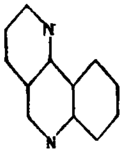
II.



III.



D. *Quinoquinolines* are obtained from the *γ*-amidoquinolines:



In their chemical behavior all of these bases resemble the quinolines.

A. *α*-**Naphthoquinoline**, $C_{13}H_9N$, melts at 52° and boils at 251°., *β*-**Naphthoquinoline** melts at 93°. The latter is obtained from the *β*-naphthylamines substituted in the *α*-position by bromine or NO_2, through the splitting-off of the substituents. Potassium permanganate converts the naphthoquinolines into two phenylpyridine dicarboxylic acids (p. 531). The hydrides of the naphthoquinolines are noteworthy. In using tin and hydrochloric acid the pyridine nucleus, as in the case of quinoline, is hydrogenized:

Tetrahydro-(*α*)-naphthoquinoline, $C_{10}H_6<\begin{matrix}CH_2-CH_2\\ NH-CH_2\end{matrix}$, melting at 46°, and the *β-body*, melting at 63°, behave like *alkylic α-* and *β-naphthylamines*. Sodium and boiling amyl alcohol produce **ar-Octohydro-(*α*)-naphthoquinoline**,

$\begin{matrix}CH_2-CH_2\\ CH_2-CH_2\end{matrix}>C_6H_2<\begin{matrix}CH_2-CH_2\\ NH-CH_2\end{matrix}$, melting at 48° and boiling at 216° (37 mm.), and

the *β-compound*, melting at 60° and boiling at 325° (717 mm.). In these bodies not only the pyridine nucleus, but also the outer benzene nucleus, has taken up hydrogen atoms, which accounts for their *aromatic benzene amine*—alkylic aniline—*character*. From β-naphthoquinoline there is simultaneously formed an isomeric ac-**Octohydro**-(β)-**naphthoquinoline**, $\begin{array}{l} CH_2 - CH_2 - CH - CH_2 - CH_2 \\ \vert \qquad\qquad\qquad\; \vert \qquad\qquad\quad\; \vert \\ C_6H_4 \text{———————} CH - NH - CH_2 \end{array}$, melting at 91° and boiling at 321°, in which the middle benzene nucleus is hydrogenized. It therefore corresponds to decahydroquinoline and possesses the properties of a piperidine.

B. **Anthraquinoline**, $C_{17}H_{11}N$, melts at 170° and boils at 446°. Its solutions exhibit an intense blue fluorescence. Chromic acid oxidizes it to **anthraquinone quinoline**, corresponding to anthraquinone. Its dioxy-compound is

Alizarin Blue, Dioxyanthraquinone quinoline,

$C_6H_4{<}{}^{CO}_{CO}{>}C_6(OH)_2{<}\begin{array}{l} CH = CH \\ N \;\; = \overset{\vert}{C}H \end{array}$, melting at 270°. It consists of metallic, bluish-violet-colored needles. It is produced when m-nitro-alizarin or amido-alizarin is heated with glycerol and sulphuric acid (B. **18**, 445; **29**, 708). It unites with acids and bases to form salts. It occurs in trade in the form of a bluish-violet paste, and, like alizarin, is applied in dyeing. Since reducing agents decolorize it (zinc-dust, grape sugar) and it again separates on exposure to the air, it is adapted to the vat-dyeing.

By the action of sulphuric acid more hydroxyl groups are introduced into alizarin-blue. The products are *alizarin-blue green*, *alizarin-green*, *alizarin-indigo-blue*. These are mixtures of sulpho-acids of tri-, tetra-, and penta-oxyanthraquinone quinolines (B. **26**, R. 711).

C. (m)-**Phenanthroline**, $C_{12}H_8N_2(+ 2H_2O)$, melting at (65°) 78°, is obtained from meta-diamidobenzene or 2-amidoquinoline (B. *16*, 2519; *23*, 1016). p-**Phenanthroline, Pseudophenanthroline**, is derived from p-diamidobenzene or amidoazobenzene with glycerol and sulphuric acid. It melts at 173°. Potassium permanganate oxidizes the phenanthrolines to α,β- and β,β-dipyridyl dicarboxylic acids (B. **24**, 2623).

α-**Methyl-o-phenanthroline**, $C_{12}H_7(CH_3)N_2(+ 2H_2O)$, melting at (53°) 76°, is prepared from 1-amidoquinaldine (B. **22**, 253).

D. α-**Methyl-γ-quinoquinoline**, $C_{12}H_7(CH_3)N_2$, melting at 206° and boiling at 360°, is prepared from γ-amidoquinaldine, glycerol, sulphuric acid, and nitrobenzene (B. **27**, R. 632).

IV. ISOQUINOLINE GROUP.

While quinoline or benzopyridine results from pyridine by the attachment of the benzene nucleus to its carbon atoms occupying the α,β-positions, the formula of the isomeric isoquinoline or isobenzopyridine is produced by the benzene nucleus joining itself to the β,γ-C-atoms of pyridine. Its *nitrogen* member is therefore separated from the benzene nucleus by a methine group:

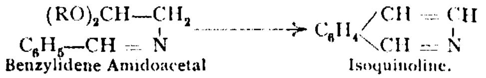
Quinoline **Isoquinoline.**

This constitution seems evident from the oxidation of isoquinoline to β,γ-pyridine dicarboxylic acid, as well as from the methods by which it is obtained synthetically.

Quinoline is similar to isoquinoline in its deportment. It is found with it in coal-tar (Hoogewerff and van Dorpp, 1885). It is the mother substance of a class of important alkaloids belonging to the opium bases —*e. g.*, *papaverine*, *narcotine*, *hydrastine*, etc. (p. 578).

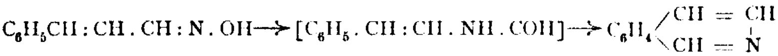
Syntheses of Isoquinoline Derivatives:

1. Isoquinolines are produced by ring-formation from benzene compounds of the constitution $C_6H_5—C—N—C—CO$ or $C_6H_5—C—C—N—CO$. For example, *isoquinolines* are formed on digesting benzylidene amidoacetal or benzylamidoacetaldehyde with sulphuric acid (B. **27**, R. 628; **28**, 764):



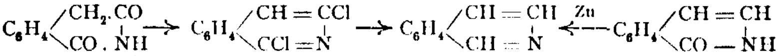
Benzylidene Amidoacetal — Isoquinoline.

a-Methyldihydroquinoline (B. **26**, 1904) is obtained from acetphenethylamide, $C_6H_5.CH_2.CH_2.NHCOCH_3$. *Trichlorisoquinoline* is produced by the action of PCl_5 upon *hippuramide*, $C_6H_5.CO.NH.CH_2.CONH_2$, just as malonanilic acid, $C_6H_5NH.CO.CH_2.COOH$, under like treatment yields trichlorquinoline (p. 547). The formation of isoquinoline from cinnam aldoxime and from benzylidene acetoxime upon heating them with P_2O_5 is remarkable (B. **27**, 2795; **28**, 818). It will be necessary to assume here an atomic rearrangement similar to that in the Beckmann transposition:



Cinnam-aldoxime — Isoquinoline.

2. The linking oxygen atom in the lactones of the formula $C_6H_4<\begin{matrix}CR = CR_1 \\ CO — O\end{matrix}$, so-called isocoumarins, can readily be exchanged for the NH-group by means of cold aqueous ammonia. The products are isoquinolines or isocarbostyrils, which by successive treatment with PCl_5 and HI and phosphorus, or with zinc-dust, are converted into isoquinolines. Homophthalides and homologous homophthalides, under similar treatment, are also changed to isoquinolines (B. **21**, 2299; **25**, 1138, 1493, 3563; **26**, 1842):



Homophthalimide — a,β-Dichlorisoquinoline — Isoquinoline — Isocarbostyril.

Isoquinoline, C_9H_7N, melting at 23° and boiling at 240.5°, is very similar to quinoline. It occurs, together with ordinary quinoline, in the crude quinoline from coal-tar. It is separated from the accompanying compounds by the crystallization of the sulphates (B. **18**, R. 384). In addition to the methods given above it is also produced by distilling benzylidine ethylamine, $C_6H_5.CH:N.CH_2.CH_3$, through tubes heated to redness (B. **25**, 734). Potassium permanganate oxidizes it to phthalic acid (destroying the pyridine nucleus) and β,γ-pyridine dicarboxylic acid (by destroying the benzene nucleus).

Alkylic phthalic acid imides are produced from the halogen alkyl addition products of isoquinoline (B. **31**, R. 786).

Its *iodmethylate*, $C_9H_7N.ICH_3$, melting at 159°, is changed, like the quinolinium and pyridinium iodides (p. 530), by potassium ferricyanide and sodium hydroxide into n-methyl isoquinolon (B. **26**, R. 270). Nitric acid changes isoquinoline into a Bz-nitroisoquinoline, melting at 110° (B. **29**, R. 792). **2,3-Methylene Dioxyisoquinoline,** $(CH_2O_2)C_6H_2(C_3H_3N)$, melting at 124°, is obtained from piperonal acetalamine,

and upon reduction yields tetrahydro-2,3-methylenedioxyisoquinoline or hydrohydrastinine (p. 578; A. **286**, 1).

Bz-1- and 3-**Methyl Isoquinolines**, boiling at 258° and melting at 83°, and boiling at 264°, are prepared from o- and p-methylbenzylidene amidoacetal (C. 1897, I, 865).

α-**Methyl Isoquinoline**, $C_9H_6(CH_3)N$, boiling at 248° (its *sulphate* at 247°), results from the action of sulphuric acid upon acetophenone amidoacetal (B. **27**, R. 628). It is probably identical with the methyl isoquinoline isolated from *papaveroline* (B. **23**, R. 653). β-**Methyl Isoquinoline**, melting at 68° and boiling at 246°, is produced when methyl isocarbostyril is distilled with zinc-dust. γ-**Methyl Isoquinoline**, boiling at 256°, is formed when dimethylhomophthalimide is distilled with zinc-dust (B. **21**, 2300). β-**Ethyl Isoquinoline**, $C_9(C_2H_5)H_6N$, boiling at 256°, and β-**Phenyl Isoquinoline**, $C_9(C_6H_5)H_6N$, melting at 104°, are obtained from ethyl- and phenyl isocarbostyril (B. **25**, 3573; **27**, 2237). α-**Phenyl Isoquinoline**, melting at 88°, is derived from benzophenone imido-acetal, $(C_6H_5)_2C:NCH_2CH(OC_2H_5)_2$ (C. 1897, I, 865).

A beautiful red dye—**Quinoline Red**—is produced by condensing benzotrichloride with quinaldine and isoquinoline when they are heated with zinc chloride. This compound has a constitution analogous to that of malachite green (B. **20**, 4).

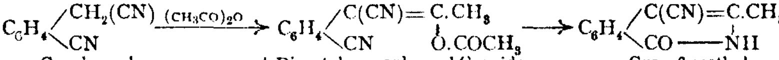
In addition to its coloring properties, it possesses the remarkable power of rendering photographic plates orthochromatic.

Isoquinolines, with halogens in the pyridine nucleus, result when PCl_5 acts upon the isocarbostyrils (below) and homophthalimides (p. 244). Chlorine atoms in the α-position have the same reactivity as the chlorine atoms in the α- or γ-position of quinoline (p. 547).

β-**Chlorquinoline**, C_9H_6ClN, melting at 48° and boiling at 281°, is produced by the partial reduction of α,β-**dichlorisoquinoline**, $C_9H_5Cl_2N$, melting at 122° and boiling at 306°, which is produced on treating homophthalimide with $POCl_3$ (B. **19**, 2355).

α-**Chlor**-β-**methyl** and α-**Chlor**-β-**phenyl Isoquinolines**, melting at 36° and 77°, are obtained from the corresponding isocarbostyrils. The latter combines with aniline to α-**Anilido**-β-**phenyl Isoquinoline**, $C_9H_5(NHC_6H_5)N$, melts at 126° (B. **25**, 2709).

Oxyisoquinolines, isocarbostyrils, are metameric with the carbostyrils (below). They result from the action of ammonia upon isocoumarins (p. 555). Another universal method of producing the isocarbostyrils consists in rearranging the reaction products of acid anhydrides and o-cyanbenzyl cyanide (p. 286) with alkalies:



o-Cyanbenzyl Cyanide — ψ-Diacetyl-o-cyanbenzyl Cyanide — γ-Cyan-β-methyl Isocarbostyril.

The alkyl cyanisocarbostyrils produced in this way are readily decomposed by concentrated sulphuric acid. The cyanogen group is eliminated and β-alkylic isocarbostyrils result (B. **27**, 827, 2232; **29**, 2543).

Isocarbostyrils, like the carbostyrils, yield ethers of the hydroxyl and keto-forms. The latter are obtained from isocarbostyrils and alkyl iodides, while the former are mostly made through the interaction of α-chlorisoquinolines and sodium alcoholates.

Isocarbostyril, α-**Isoquinoline**, C_9H_7ON (p. 286), results from isocoumarin and ammonia, and from **isocarbostyril carboxylic acid**, $C_9H_6ON.COOH$, a reaction-product of ammonia and isocoumarin carboxylic acid, by the elimination of CO_2.

α-**Methoxyisoquinoline**, $C_6H_4\left\langle\begin{array}{l}CH = CH \\ C(OCH_3) = N\end{array}\right.$, boiling at 240°, is produced by the interaction of the silver salt of isocarbostyril and methyl iodide. The isomeric n-**Methyl**-α-**isoquinoline**, $C_6H_4\left\langle\begin{array}{l}CH = CH \\ CO - N(CH_3)\end{array}\right.$, melting at 54° (40°: B. **26**, R. 270; **27**, 205), is obtained from isocarbostyril, methyl iodide, and alkalies (B. **26**, R. 236), or by the action of alkaline potassium ferricyanide upon methyl isoquinolinium iodide (p. 555); other n-alkyl isoquinolons are produced by the action of primary amines upon isocoumarin (B. **27**, 198), or its carboxylic acid. β-**Methyl Isocarbostyril**, $C_9(CH_3)H_6ON$, melts at 211°; β-**ethyl isocarbostyril melts at 141°**; β-**isopropyl isocarbostyril**

melts at 221° (B. 29, 2393). **β-Phenyl Isocarbostyril**, *isobenzal phthalimidine*, melting at 197°, also results from the action of ammonia upon isobenzalphthalide (B. 18, 2448; 27, 2237).*

A **bz-2,3,4-Trioxy-γ-methyl Isocarbostyril**, $C_6H(OH)_3 : [C_3H_2(CH_3)ON]$, is derived from the corresponding isocoumarin derivative, which is produced when concentrated sulphuric acid acts upon gallacetol, $C_6H_2(OH)_3 . CO . O . CH_2 . COCH_3$ (B. 26, 419).

Hydroisoquinolines.—1. *Dihydroïsoquinolines:* **o-Methyl Dihydroisoquinoline**, $C_9H_8(CH_3)N$, boiling at 237–241°, and **α-Phenyldihydroisoquinoline**, $C_9H_8(C_6H_5)N$, melting at 195°, result when P_2O_5 or $ZnCl_2$ acts upon phenyl ethyl acetamide and phenethyl benzamide, $C_6H_5CH_2 . CH_2 . NHCO . C_6H_5$.

The n-alkyl derivatives of the isocarbostyrils are ketodihydroïsoquinolines.

2. *Tetrahydroïsoquinolines:* They are produced when isoquinoline is reduced with tin and hydrochloric acid, or, better, with sodium and alcohol. The pyridine nucleus is hydrogenized. Tetrahydroïsoquinoline shows the properties of the alkylic benzylamines, while tetrahydroquinoline manifests those of an alkylic aniline:

$$C_6H_4\left\langle\begin{matrix}CH_2-CH_2\\ \vert \\ NH-CH_2\end{matrix}\right. \qquad C_6H_4\left\langle\begin{matrix}CH_2-CH_2\\ \vert \\ CH_2-NH\end{matrix}\right.$$

Tetrahydroquinoline   Tetrahydroïsoquinoline.

Tetrahydroïsoquinoline, $C_9H_{11}N$, boiling at 233°, is a powerful base, which absorbs carbon dioxide from the air and reduces warm ammoniacal silver solutions. Its *nitroso*-compound melts at 33°. The *iodmethylate* of n-**methyl tetrahydroïsoquinoline**, $C_9H_{10}N(CH_3)_2I$, melting at 189°, is obtained from methyl iodide and tetrahydroïsoquinoline. n-**Benzoyl Tetrahydroïsoquinoline**, boiling at 245° to 250° (50 mm.), is converted by $KMnO_4$ into ω-benzoylamidoethyl-o-benzoic acid,

$$C_6H_4\left\langle\begin{matrix}CH_2 & - & CH_2\\ & & \vert \\ COOH & & NHCOC_6H_5\end{matrix}\right.$$

(p. 539). The latter readily parts with water and becomes the benzoyl derivative of—

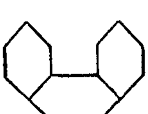
Hydroisocarbostyril, *Ketotetrahydroïsoquinoline*, $C_6H_4\left\langle\begin{matrix}CH_2-CH_2\\ \vert \\ CO-NH\end{matrix}\right.$, melting at 71° (B. 26, 1220).

The homophthalimides—*e. g.*, $C_6H_4\left\langle\begin{matrix}CH_2-CO\\ \vert \\ CO-NH\end{matrix}\right.$ (p. 244)—are *diketotetrahydroïsoquinolines*.

The alkaloids *berberine*, *hydrastine*, *narcotine* (p. 577), are derivatives of tetrahydroisoquinoline.

V. PHENANTHRIDINE.

It can be considered both as a benzo-derivative of quinoline and of isoquinoline. It results also from phenanthrene by replacing one of the intermediate —CH= groups by nitrogen:



It is isomeric with the naphthoquinolines (p. 553).

Phenanthridines are produced upon heating the acidyl derivatives of o-amidodiphenyl (B. 29, 1182):

$$\begin{matrix}C_6H_5 & OCH\\ \vert & \vert \\ C_6H_4 & -NH\end{matrix} \longrightarrow \begin{matrix}C_6H_4-CH\\ \vert \quad \Vert \\ C_6H_4-N\end{matrix} ; \quad \begin{matrix}C_6H_5 & OCCH_3\\ \vert & \vert \\ C_6H_4 & -NH\end{matrix} \longrightarrow \begin{matrix}C_6H_4-CCH_3\\ \vert \quad \Vert \\ C_6H_4-N\end{matrix} .$$

Phenanthridine, $C_{13}H_9N$, melting at 104° and boiling above 360°, results in the pyrogenic way from benzylidene aniline :

$$C_6H_5CH = NC_6H_5 \xrightarrow{-2H} \overline{C_6H_4CH = NC_6H_4};$$

and when phenanthridone is distilled with zinc-dust. Bleaching lime and cobalt re-oxidize it to phenanthridone (B. **26**, 1964), while tin and hydrochloric acid reduce it to **dihydrophenanthridine**, $\overline{C_6H_4CH_2 - NHC_6H_4}$, melting at 90° (A. **266**, 142).

ms-**Methyl-**, **ethyl-**, and **phenyl-phenanthridine** melt at 85°, 55°, and 109° (B. **29**, 1184).

Phenanthridone, $\overline{C_6H_4CO . NHC_6H_4}$, melting at 293°, is produced on treating diphenamic acid with bromine and caustic potash :

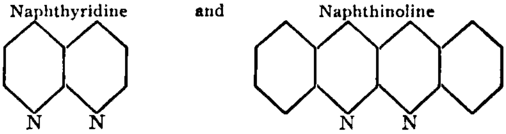
$$C_6H_4\langle_{CONH_2\ \ COOH}\rangle C_6H_4 \longrightarrow C_6H_4\langle_{NH_2\ \ COOH}\rangle C_6H_4 \longrightarrow C_6H_4\langle_{NH-CO}\rangle C_6H_4,$$

as well as by the *rearrangement of o-amidophenylene ketone* (p. 418), *on fusion with* caustic potash ; by transposition of diphenylene ketone oxime with zinc chloride, and, finally, from o-diphenyl urethane, $C_6H_5C_6H_4NHCO_2C_2H_5$, on digesting it with zinc chloride (B. **26**, R. 712 ; **28**, R. 455 ; **29**, 230, 1188). Phenanthridone and phosphorus pentachloride yield *chlorphenanthridine*, $\overline{C_6H_4CCl = NC_6H_4}$, melting at 116°. n-**Methyl Phenanthridone**, $C_{13}H_8ONCH_3$, melting at 108°, is formed in the action of alkaline potassium ferricyanide upon *methyl phenanthridinium iodide*, $C_{13}H_9N . ICH_3$ (B. **26**, 1962 ; compare pyridinium and quinolinium compounds, pp. 530, 544).

VI. NAPHTHYRIDINE, NAPHTHINOLINE.

The union of two pyridine nuclei or of two quinoline nuclei in the manner of naphthalene gives rise to the hypothetical parent substances:

Naphthyridine and Naphthinoline



Thus far only hydrides of these bodies have been prepared.

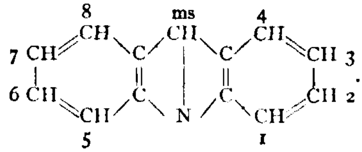
Octohydronaphthyridine, $C_8H_{14}N_2$ (forms a *platinum salt*), melts at 227°, and is prepared from γ,γ-diamidodipropyl acetic acid (B. **26**, 2137) :

$$\begin{matrix} CH_2-CH_2-CH_2-CH-CH_2-CH_2-CH_2 \\ | \qquad\qquad\quad | \qquad\qquad\quad | \\ NH_2 \qquad O:COH \qquad NH_2 \end{matrix} \longrightarrow \begin{matrix} CH_2-CH_2-CH_2-CH-CH_2-CH_2-CH_2 \\ | \qquad\qquad\quad | \qquad\qquad\quad | \\ N \overline{\overline{\qquad\qquad}} C \text{———} NH \end{matrix}$$

Tetrahydronaphthinoline, $C_{16}H_{14}N_2$, melting at 212°, is formed by the reduction of o_2-dinitrobenzylacetic acid, $\begin{matrix} C_6H_4-CH_2-CH-CH_2-C_6H_4 \\ | \qquad\quad | \qquad\quad | \\ NO_2 \qquad OCOH \qquad NO_2 \end{matrix}$ (p. 379), in a manner similar to that of the naphthyridine body. Mercury acetate oxidizes it very easily to *dihydronaphthinoline*, $C_{16}H_{12}N_2$, melting at 201°, the salts of which show an intense green fluorescence. It is reduced by sodium amalgam in glacial acetic acid solution to *hexahydronaphthinoline*, $C_{16}H_{16}N_2(+1\frac{1}{2}H_2O)$, melting at 128° (B. **27**, 2244).

VII. ACRIDINE GROUP.

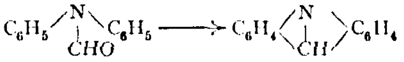
Acridine represents an anthracene, one of the intermediate CH-groups of which is replaced by nitrogen:



Its relations to quinoline and pyridine follow from its oxidation to quinoline dicarboxylic acid and pyridine tetracarboxylic acids (pp. 549, 538).

Acridine occurs in the crude anthracene of coal-tar. Different of its derivatives are important technically as dyes. Acridines may be synthesized:

1. From diphenylamine and acids, or from the acidyl derivatives of diphenylamine, if they be heated together with zinc chloride. This is analogous to the formation of the phenanthridines from acidyl-o-amido-diphenylenes (p. 557) (Bernthsen, A. **224**, 1):



Formyl Diphenylamine — Acridine.

This reaction is a certain proof of the para-union in acridine.

Homologous acridines are similarly obtained from diphenylamine and the higher fatty acids. In them the hydrogen of the CH-group is replaced by alkyls. They are called meso-derivatives (B. **18**, 690; **25**, R. 940). The substituted diphenylamines (B. **24**, 2039), ditolylamine, phenylnaphthylamine, etc., react just like diphenylamine.

2. Various acridine compounds have been prepared from the o-amido-derivatives of di- and tri-phenylmethane (B. **26**, 3085):

o-Amidodiphenyl Methane — Acridine.

3. Acridones are prepared from the alphylanthranilic acids (B. **26**, R. 712; **27**, R. 642), just as anthraquinone is obtained from benzoyl benzoic acid:

Phenylanthranilic Acid — Acridone,

or by the action of phenols (naphthols, etc.) upon acetanthranilic acid (B. **25**, 1983, 2740).

The acridines are very stable compounds. They are more feeble bases than the pyridines and quinolines. They combine with alkyl iodides to alkyl acridinium iodides, which are converted by alkaline potassium ferricyanide (similar to the pyridinium and quinolinium iodides) into n-alkyl acridones. When the acridines are reduced they become dihydroacridines, which readily revert to the acridines.

Acridine, $C_{13}H_9N$, melts at 110°. It sublimes at 100°. Its solutions have a blue fluorescence. It is isomeric with phenanthridine and the naphthoquinolines. In addition to the general reactions it is also produced when diphenylamine is heated with chloroform and zinc chloride to 200° (B. **17**, 101), and in the distillation of acridone with zinc-dust (B. **26**, R. 714). Potassium permanganate oxidizes it to *acridic acid*, or quinoline-α,β-dicarboxylic acid, from which it was concluded that quinoline and pyridine had the diagonal formula (pp. 526, 541) (Riedel, B. **16**, 1612).

In the oxidation of the acridinium compounds the heterocyclic nucleus is ruptured and phenylamidobenzoic acid, $C_6H_5.NH.C_6H_4.COOH$, is produced.

ms-**Methyl Acridine**, $C_{13}H_8(CH_3)N$, melting at 114°, is obtained from acetyldiphenylamine. Like quinaldine (p. 546) and picoline (p. 531) it combines with chloral to $C_{13}H_8NCH_2CH(OH)CCl_3$. This is converted by alkalies into ms-*acridyl-acrylic acid*, $C_{13}H_8NCH:CH.COOH$, which potassium permanganate oxidizes to *acridyl aldehyde*, $C_{13}H_8NCHO$, and the latter to ms-*acridyl carboxylic acid*, $C_{13}H_8NCOOH$ (B. **20**, 1541).

ms-**Phenyl Acridine**, $C_{13}H_8(C_6H_5)N$, results upon heating diphenylamine and benzoic acid. It crystallizes from benzene, with one molecule of benzene. It melts at 181°.

Chrysaniline, ms-p-Amidophenyl-2-amidoacridine,

$NH_2C_6H_3\left\langle\begin{matrix}C(C_6H_4NH_2)\\ | \\ N\end{matrix}\right\rangle C_6H_4$, melting at 268°, is the chief constituent of the beautiful yellow dye, *phosphin*, which is obtained as a by-product in the rosaniline manufacture. It forms red-colored salts; these dye silk and wool a beautiful yellow. Their solutions exhibit a beautiful yellow-green fluorescence.

The formation of chrysaniline from pararosaniline proceeds, evidently, according to the diagram of method 2 for the acridines.

Dihydroacridine, $C_6H_4{<}^{CH_2}_{NH}{>}C_6H_4$, is formed when acridine is reduced with zinc-dust and hydrochloric acid. It *no longer* manifests basic properties, and melts at 168°. It reduces ammoniacal silver nitrate with the reformation of acridine.

Acridone, *ketodihydroacridine*, $C_6H_4{<}^{CO}_{NH}{>}C_6H_4$, melting at 354°, can be distilled. It is formed when sulphuric acid at 100° acts upon phenyl anthranilic acid, and by the dry distillation of the anilide of salicylic acid, when it may be assumed that the latter first rearranges itself to phenyl anthranilic acid. The salicyl toluides also yield methylated acridones (B. **29**, 1189). PCl_5 converts it into *chloracridine*, $C_6H_4\left\langle\begin{matrix}CCl\\ | \\ N\end{matrix}\right\rangle C_6H_4$, melting at 119°. With methyl iodide and caustic potash it forms n-**Methyl Acridone**, $C_6H_4\left\langle\begin{matrix}CO\\ N(CH)_3\end{matrix}\right\rangle C_6H_4$, melting at 203°, which is also produced when caustic potash and potassium ferricyanide act upon methyl acridinium iodide. Acridine is formed when acridone is heated with zinc-dust. Sodium and alcohol convert it into dihydroacridine. The following are obtained in the same way as acridone:

4-Methyl Acridone, $CH_3.C_6H_3.\left(\begin{matrix}CO\\ NH\end{matrix}\right)C_6H_4$, melting at 346°;
2-Methyl Acridone, melting at 338°;
2,4-Dimethyl Acridone, melting at 297° (B. **27**, R. 642);
Phenonaphthacridone, $C_6H_4{<}^{CO}_{NH}{>}C_{10}H_6$; and
Dinaphthacridone, $C_{10}H_6{<}^{CO}_{NH}{>}C_{10}H_6$ (B. **25**, 2744).

Peculiar acridine derivatives have been obtained by the condensation of acidyl carbazoles (B. **24**, R. 829; **25**, R. 114):

Benzoyl Carbazole — ms-Phenylcarbazacridine, m. p. 186°.

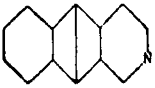
Quinacridine, $C_6H_4<{CH \atop N}>C_6H_2<{CH \atop N}>C_6H_4$, melting at 213°, is a compound which was obtained in the zinc-distillation of an oxygen-containing body—**oxyquinacridone**. The latter results upon heating phloroglucin with anthranilic acid:

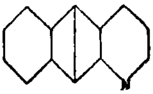
$$2C_6H_4<{COOH \atop NH_2} + C_6H_6O_3 \longrightarrow C_6H_4<{CO \atop NH}>C_6H(OH)<{CO \atop NH}>C_6H_4.$$

It does not fuse. It begins to decompose above 400°. It is insoluble in almost all solvents. Sodium amalgam reduces quinacridine to **tetrahydroquinacridine**, melting at 272° (B. **29**, 76).

VIII. ANTHRAPYRIDINES.

The α- and β-anthrapyridines are isomeric with acridine:





α-**Anthrapyridine**, $C_{13}H_9N$, melting at 275°, results from the reduction of α-**anthrapyridine quinone**, $C_6H_4<{CO \atop CO}>C_5H_3N$, melting at 280°, which is made by condensing β-benzoyl picolinic acid with sulphuric acid. β-**Anthrapyridine**, melting at 166°, is similarly formed from β-**anthrapyridine quinone**, the condensation product of γ-benzoyl nicotinic acid (B. **28**, 1658).

ALKALOIDS.*

Formerly, all nitrogen-containing bodies occurring in plants, and possessing basic, alkaline character, or derivatives of the same, from which bases could be isolated, were designated as alkaloids.

Many of them (betaïne, asparagine, theïne; I, 310, 490, 515) have, in accord with their constitution, been already discussed with the various amido-derivatives; the most of those remaining which have been studied recently show themselves to be derivatives of pyridine, quinoline, and isoquinoline, or of their corresponding hydro-derivatives. Several have been prepared artificially (*piperine*, *conine*, *trigonelline*, and *arekaïdine*); in the case of others, synthesis has had the way made plain by analysis, or it has been attained, as in the case of *hydrastine*, for the basic decomposition product of the alkaloid. Like the benzene derivatives, they have much in common in their whole deportment. They are the chief

* Consult "La Constitution chimique des Alcaloïdes végétaux," par Amé Pictet. Paris, G. Masson, 1897 (II. ed.).

constituents of the active principles of the vegetable drugs employed as medicines or poisons.

Because of their great number and their ofttimes unusually remarkable physiological and pharmacological properties they constitute one of the most interesting classes of carbon compounds.

Occurrence.—The vegetable alkaloids occur almost exclusively in the dicotyledons; but *one*, the poorly investigated *colchicine*, is formed in a monocotyledon, while the large families of the Compositæ and Labiatæ do not furnish them. In plants they are generally combined with widely distributed *plant acids*—*e.g.*, *malic acid* (I, 487), *citric acid* (I, 529), and *tannic acid* (p. 543). Many are accompanied by acids which usually are found associated with definite alkaloids—*e. g.*, the opium alkaloids are united with meconic acid (p. 523), and the quinia alkaloids with *quinic acid* (p. 301). The alkaloids prized for their pharmacological properties are the subject of technical isolation. The artificially prepared carbon compounds, having similar physiological action, hold a subordinate position compared with them—*e. g.*, quinine and *antipyrine* (p. 488); atropine and several *tropeïnes* (p. 567); cocaïne and *eucaine* (p. 540).

Some alkaloids contain no oxygen, and then are generally liquid and volatile—*e. g.*, *piperidine*, *conine*, *nicotine*, and *sparteïne*. Most of them do, however, contain that element, and are solid and non-volatile. Nearly all are tertiary amines; some, however (like the hydrides of the pyridine nucleus, belong to the secondary amines. Many (like *pilocarpine*) are ammonium bases. Tannic acid, phospho-molybdic acid, platinic chloride, and many double salts (like $HgI_2 . KI$) precipitate all these bases from their aqueous solutions. The bases are regained from these compounds by alkalies.

The alkaloids have a more or less bitter taste. Most of them are optically active and, indeed, lævorotatory (I, 67). *Conine*, *narcotine*, and *pilocarpine* are dextrogyratory. Piperine is inactive. Many alkaloids give characteristic colors with chlorine water, nitric acid, or concentrated sulphuric acid.

I. THE PYRIDINE GROUP OF THE ALKALOIDS.

Piperine, $C_{17}H_{19}NO_2 = CH_2\langle{}^{CH_2-CH_2}_{CH_2-CH_2}\rangle N.CO.CH{:}CH.CH{:}CH[1]C_6H_3\left\{{}^{[3]O}_{[4]O}\right\rangle CH_2$ melting at 128°, occurs in different varieties of pepper, the fruit of *Piper nigrum* and *Piper longum*. It dissolves with a deep red color in sulphuric acid. It is decomposed by boiling alcohol into piperidine and piperic acid.

The two decomposition products of piperine have been built up from their elements, and by allowing the chloride of piperic acid to act upon piperidine the synthesis of piperine itself has been realized (B. **27**, 2958). The synthesis of conine presupposes that of piperidine, and is represented by diagram under conine. Artificial piperines have been prepared from the synthetic α-alkyl and α-phenyl piperic acids with the assistance of the chlorides (B. **28**, 1195).

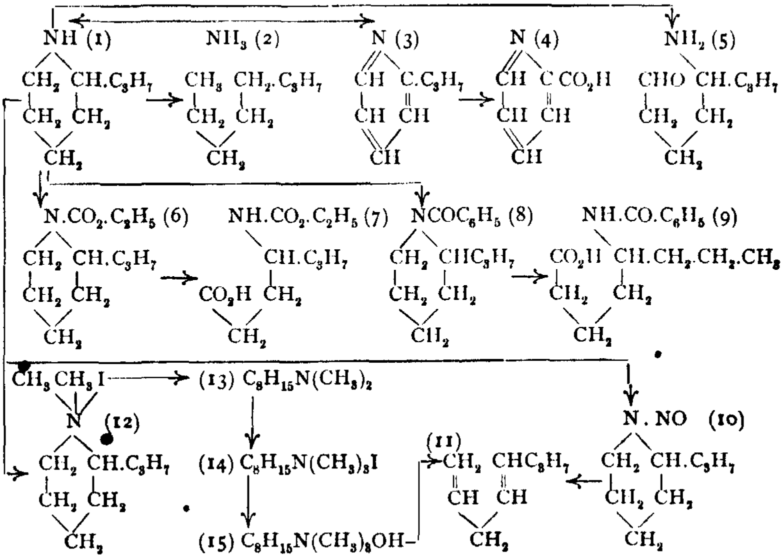
α-**Conine,** d,α,n-*propylpiperidine*, $C_8H_{17}N = CH_2\langle{}^{CH_2-CH-CH_2.CH_2.CH_3}_{CH_2-CH_2}\rangle NH$, boiling at 167°, with sp. gr. 0.886 (0°), $[\alpha]_D = +18.3$ (B. **27**, 3062), occurs together with n-methyl conine and γ-coniceïne, $CH_2\langle{}^{CH\ =C(C_3H_7)}_{CH_2-CH_2-}\rangle NH$ (B. **28**, 302), conhydrin, and pseudoconhydrin

(p. 564), in hemlock (*Conium maculatum*), especially in the seeds. It is a colorless liquid with a stupefying odor. It is a very powerful poison.

History: Giesecke (1827) discovered conine. A. W. Hofmann (1881) determined its molecular magnitude, and in 1884 demonstrated that it yielded conyrine or α-propyl pyridine upon distillation with zinc-dust. Obtaining picolinic acid by oxidation, he thus proved the α-position of the propyl group. The synthesis of optically inactive conine, its decomposition into d- and l-conine, and thereby the first complete synthesis of an optically active alkaloid, are due to Ladenburg (1886) (B. 22, 1403).

The following diagrams represent the decomposition of conine, which corresponds to that of piperidine (p. 539), and also the synthesis which presupposes that of piperidine and pyridine.

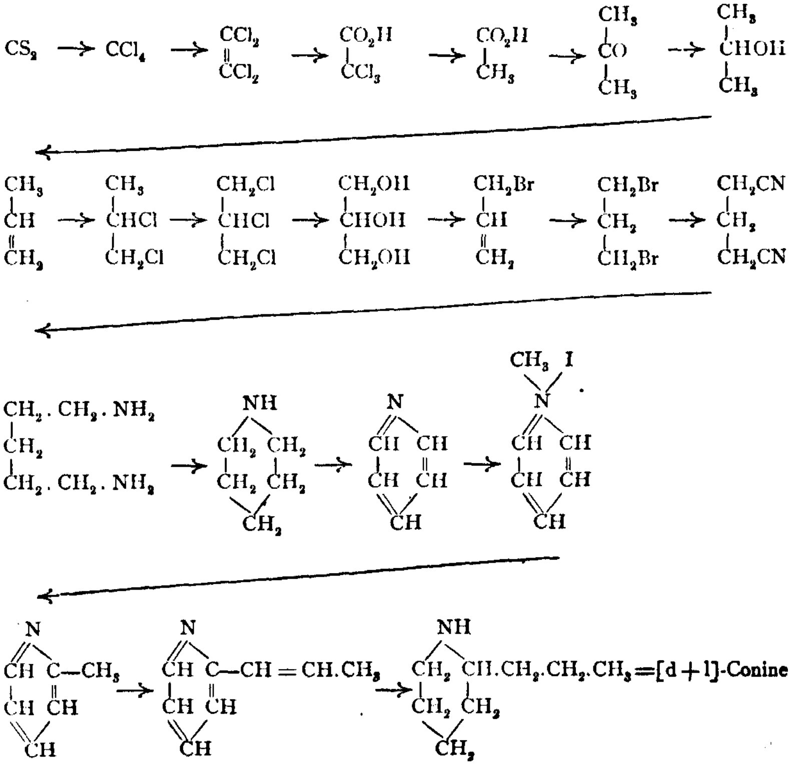
Decomposition of Conine: The reduction of natural d-conine (1) by hydriodic acid resolves it into n-octane (2) and ammonia (B. 18, 13). The distillation with zinc-dust leads to conyrine (3), or α,n-propyl pyridine, which hydriodic acid reduces to inactive [d + l]-conine, while upon oxidation it becomes picolinic acid (4) or pyridine-α-carboxylic acid. Hydrogen peroxide oxidizes conine to δ-amido-n-octyl aldehyde, or δ-propylamidovaleraldehyde (5) (B. 28, 1460). Nitric acid oxidizes conylurethane (6) to carbethoxyconinic acid or γ-carboethylamido-n-heptan acid (7) (B. 15, 1947), which yields coninic acid when heated with hydrochloric acid. Potassium permanganate oxidizes benzoyl conine to benzoyl homoconinic acid or δ-benzoylamido-n-octan acid (8) and benzoyl-α-amidovaleric acid (9) (B. 19, 502). Nitrous acid converts conine into nitroso-conine (10), which breaks down, on heating with phosphorus pentoxide, into water, nitrogen, and conylene (11). Methyl iodide and conine combine to dimethylconinium iodide (12), which is changed by sodium hydroxide to dimethylconine, $C_8H_{15}N(CH_3)_2$ (13) (B. 14, 708), of uncertain constitution (A. 279, 341). Dimethyl conine and methyl iodide also combine, and the resulting iodide (14) is converted by silver oxide into trimethyl conylium hydroxide, $C_8H_{15}N(CH_3)_3OH$ (15), which breaks down, upon distillation with water, into trimethylamine and conylene (10) (1, 99):



Synthesis of Conine (B. 22, 1404). We begin with the synthesis of trichloracetic acid (1, 274), which by reduction yields synthetic acetic acid (1, 244). From this we pro-

ceed to glycerol (I, 471), which can be converted into allyl bromide. Allyl bromide and hydrobromic acid combine to trimethylene bromide, the latter yielding, by the action of trimethylene cyanide, pentamethylene diamine, from which piperidine results by the elimination of ammonia (I, 314). Piperidine may be oxidized to pyridine, the iodmethylate of which—pyridinium iodide—is changed at 300° into α-picoline iodhydrate. Picoline and paraldehyde at elevated temperatures yield α-allyl pyridine, which is reduced to inactive conine.

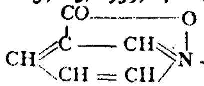
d-Conine d-tartrate separates first from a solution of dextro-tartrate of inactive conine; and caustic potash resolves it into a *conine identical* with the natural conine. As dextro-tartaric acid can be prepared from synthetic racemic acid (I, 523) the synthesis of conine is complete.



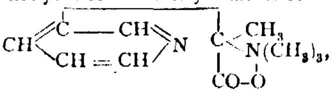
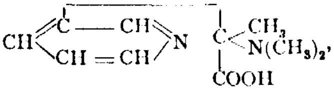
d-Conine Hydrochloride melts at 218°. **Nitroso-d-conine** is a bright yellow-colored oil. **d-Conylene Urethane** boils at 245°. **Benzoyl-d-conine** is a thick oil.

Inactive r- (racemic) or (d + l)-*conine* and l-*conine* behave physiologically and chemically like d-*conine*. Sodium and alcohol also reduce α-ethyl pyridyl ketone to (d + l)-conine. The first product is α-ethyl pyridine alkine, *α-ethyl pyridyl carbinol*, boiling at 213–218° (p. 535), then α-ethyl piperyl alkine, $C_5H_9NHCH(OH).CH_2.CH_3$, melting at 100°, identical with *pseudoconhydrine*, which has also been discovered in *Conium maculatum*. Inactive conine is best prepared by reducing γ-coniceïne (p. 538) (B. 29, 1956).

Isoconine or **Isoconicine**—consult B. **27**, R. 203; **29**, 1959, 2706 (see I, 511).

Trigonelline, *Nicotinic Acid Methyl Betaïne*,  melting at 218°, occurs in the seeds of *Trigonella fœnum græcum*, and in small amount, together with choline, in the seeds of *Pisum sativum*, and also in flax—*Cannabis sativa*. As Jahns has shown, trigonelline is identical with nicotinic acid betaïne, synthesized by Hantzsch (1886) (B. **27**, 769).

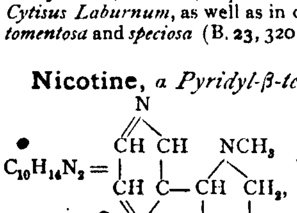
Arecaïdine, *Tetrahydronicotinic Acid Methyl Betaïne*, $C_5H_8(COO)N.CH_3(+H_2O)$, melting at 224°, occurs, together with **arecoline,** $C_8H_{13}NO_2$ (chief constituent), **arecaïne,** $C_7H_{11}NO_2$, and **guvacine,** $C_6H_9NO_2$, in the nut of *Areca Catechu*. It and its dihydro-body, **dihydroarecaïdine** or hexahydronicotinic acid methyl betaïne, have been obtained synthetically from the chlormethylate of nicotinic ester by the action of tin and hydrochloric acid. It forms **arecoline,** boiling at 209°, when treated with methyl alcohol and HCl (esterified), which by saponification yields arecaïdine, and it is therefore *tetrahydro-n-methylnicotinic methyl ester* (B. **25**, R. 198; **30**, 729). The constitution of arecaïne and guvacine has not yet been definitely established.

Pilocarpine,  $[\alpha]_D = +101.6°$, and **Pilocarpidine,**  occur in the Jaborandi leaves of *Pilocarpus pennatifolius*.

Pilocarpine is a poison which acts like nicotine (A. **238**, 230). The injection of it into milch cows occasions a very appreciable increase in the sugar of the milk (B. **26**, R. 247). When pilocarpine is treated with hydrochloric acid, or when it is boiled with water, it changes in part to pilocarpidine, and in part to β-pyridine-α-lactic acid (p. 538) and trimethylamine. Potassium permanganate oxidizes pilocarpine nitrate to β-pyridine tartronic acid, which by further oxidation becomes nicotinic acid. β-Pyridine-α-lactic acid and PBr_3 form β-pyridine-α-brompropionic acid, which trimethylamine converts at 150° into pilocarpidine. By treating pilocarpidine with methyl iodide and caustic potash, then oxidizing the methyl group, which has attached itself to the pyridine nitrogen, with silver permanganate, pilocarpine is produced (Hardy and Calmels, B. **19**, R. 703; **20**, R. 575; see B. **28**, 1762).

Cytisine, *Ulexine*, *Sophorine*, $C_{11}H_{14}N_2O$, melting at 152°, occurs in the seeds of *Cytisus Laburnum*, as well as in other Cytisus-varieties, in *Ulex europæus* and in *Sophora tomentosa* and *speciosa* (B. **23**, 3201; **24**, 634; **27**, R. 509, 884; **28**, R. 237; **29**, R. 36, 53).

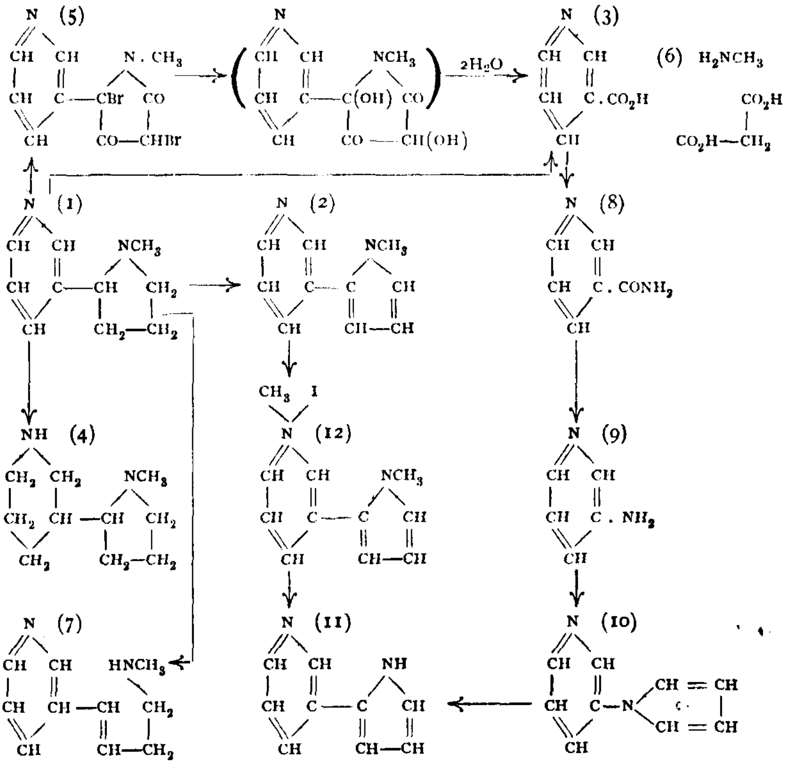
Nicotine, *α Pyridyl-β-tetrahydro-n-methyl pyrrol* (?),

 boiling at 247°, with sp. gr. 1.011 (15°), and lævogyratory (B. **26**, R. 193), occurs in the leaves of the tobacco plant, *Nicotiana tabacum*, in quantities varying from 0.6 to 8 per cent., depending upon the varieties. As a rule, the better qualities of tobacco contain less nicotine than the poorer sorts.

Nicotine is very soluble in water. It has a disagreeable odor and burning taste. It is a very violent poison.

Potassium ferricyanide, or, better, silver oxide, oxidizes nicotine (1) to nicotyrine (2) or *a*-*β*-pyridylmethyl pyrrol (?) (B. **27**, 2535). Nitric acid, chromic acid, or potassium permanganate oxidize it to nicotinic acid (3) or *β*-pyridine carboxylic acid (A. **196**, 130; see also B. **30**, 2122), while with hydrogen peroxide it yields *oxynicotine*, $C_{10}H_{14}N_2O$ (B. **28**, 456). Sodium and alcohol reduce it to hexahydronicotine (4) (B. **26**, 765). With bromine and water nicotine forms *dibromnicotine* (5) $C_{10}H_8Br_2N_2O_2$, which baryta-water resolves into methylamine, malonic acid (6), and nicotinic acid (B. **26**, 292). Nicotine takes up benzoyl chloride, with rupture, very probably, of the pyrrolidine ring. Hydrochloric acid liberates nicotine from the addition-product, while sodium alcoholate produces a secondary base, *metanicotine*, isomeric with nicotine and melting at 275–278°. It is probably *ω*-methylamido-propylidene-*β*-picoline.

History: Posselt and Reiman discovered nicotine (1828). Since 1891 Blau, but more especially Pinner, has studied its transposition reactions. The constitutional formula proposed by Pinner harmonizes with its deportment, and has more recently been fortified by the experiments of Amé Pictet and Crépieux (1895), which doubtless will eventually terminate in a synthesis of nicotine.



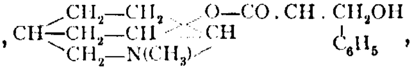
Pictet and Crépieux let potassium hypobromite act upon nicotinamide (8) and obtained *β*-amidopyridine (9), which (p. 458) becomes N,*β*-pyridyl pyrrol (10) upon distillation with mucic acid. If N,*β*-pyridyl pyrrol be conducted through tubes heated to faint redness, it is rearranged to *a*,*β*-pyridyl pyrrol (11), which methyl iodide converts very probably into nicotyrine iodmethylate (12) (B. **28**, 1909).

The preceding diagram represents a tabular view of the rearrangement reactions of nicotine and the production of nicotyrine iodmethylate from nicotinic acid.

Sparteïne, $C_{15}H_{26}N_2$, boiling at 311°, is a colorless, thick oil, occurring in *Spartium scoparium*. It is a diacid base and is a powerful narcotic. Tin and hydrochloric acid reduce it to **dihydrosparteïne,** $C_{15}H_{28}N_2$, while hydrogen peroxide oxidizes it to *mono-*, *di-*, and *trioxysparteïne* (B. **30**, 195). Hydriodic acid splits off a methyl group from sparteïne (B. **21**, 826). Diethylmethylamine, pyridine, and α-picoline are produced when it is distilled with zinc-dust (B. **26**, 3035).

II. TROPINE GROUP.

Solanum Bases.—Several very similar alkaloids are found in many varieties of solanum, of which the best known are the two isomerides: optically inactive *atropine*, discovered by Mein in 1833, as well as by Geiger and Hesse, and lævogyratory *hyoscyamine*. If they are introduced in very small quantity into the eye they cause dilatation of the pupil, and are therefore used in medicine as *mydriatics*. Both bases are found in *Hyoscyamus niger* and *albus*, in *Datura stramonium*, in the deadly nightshade, *Atropa belladonna*, and in *Duboisia myoporoides*. The less investigated bases which accompany them are *belladonine* (B. **17**, 152, 383), *hyoscine*, *scopolamine* (B. **25**, 260; **29**, 1771, 2009, 2439), *apoatropine* (below) (B. **25**, R. 573; **26**, R. 285), all of which, as acid decomposition products, yield tropic and atropic acids; as basic constituents they yield bodies closely allied to tropine.

Atropine,  , melting at 115°, is produced when the isomeric *hyoscyamine* is heated to 108.6°. This body changes in part to atropine on treatment with aqueous or alcoholic sodium hydroxide (B. **21**, 1717, 2777, 3069). It is very probable that the two bases are physical isomerides. Atropine is decomposed into *tropine* and *tropic acid*, or *α-phenylhydracrylic acid*, $CH_2OH . CH(C_6H_5)CO_2H$ (p. 252), when it is heated with hydrochloric acid or baryta-water. Conversely, atropine is formed when tropic acid and tropine are evaporated with dilute hydrochloric acid (Ladenburg).

Both the basic and the acid decomposition products of atropine contain asymmetric carbon. Indeed, tropic acid has been resolved into its optically active components, and from tropine there have been obtained with dextro- and lævo-tropic acid: *dextro-atropine*, melting at 110° to 120°, and *lævo-atropine* (B. **22**, 2590). The latter is very similar to lævo-hyoscyamine, but it is not identical with it.

Apoatropine, *Atropamine*, $C_{17}H_{21}NO_2$, melting at 60–62°, results from the action of nitric acid upon atropine. It is made synthetically by evaporating tropine atropate with dilute hydrochloric acid. It is decomposed by baryta-water into tropine and atropic acid (p. 278); it is the *tropeïne* of atropic or α-phenylacrylic acid.

Tropeïnes.—Just as tropine yields atropine with atropic acid, so it is capable of entering combination with other acids producing ester-like derivatives, which have been called *tropeïnes* (Ladenburg, A. **217**, 82; **27**, R. 202). Of these, phenylglycolyl-tropeïne, or **Homatropine,** $C_5H_7N(CH_3) . C_2H_4 . O . CO . CH(OH) . C_6H_5$, is noteworthy because its mydriatic action is not so prolonged. It is obtained from tropine and mandelic

acid. It is employed as a substitute for atropine, and is applied in the form of hydrobromide. It melts at 95.5–98.5°.

Only those tropeïnes possess mydriatic action in which the acid radical contains alcoholic hydroxyl.

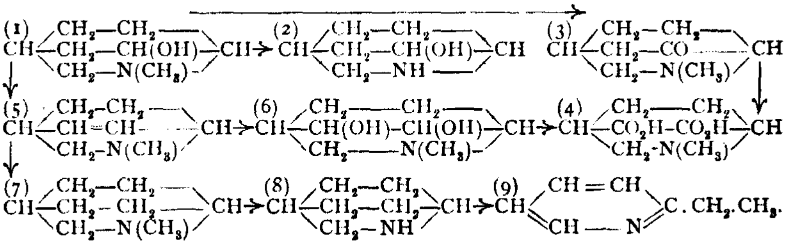
Lactyl Tropeïne melts at 74° (B. **28**, R. 492).

Benzilo-tropeïne is the tropeïne of benzilic acid (p. 367) (B. **27**, R. 202).

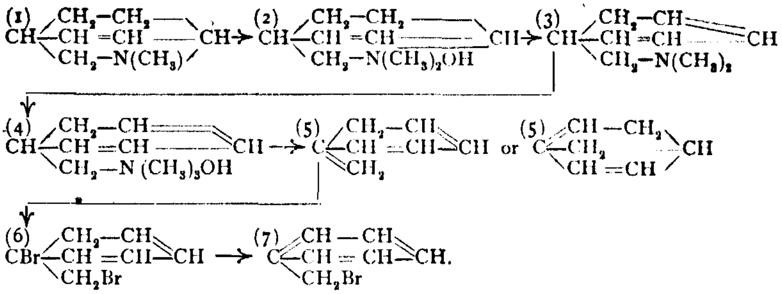
Tropine, $CH\begin{cases}CH_2-CH_2-\!-\!-\\ CH_2-CH(OH)-\\ CH_2-N(CH_3)\end{cases}CH$, melting at 62° and boiling at 233°, is the basic decomposition product of atropine. Merling regards it as an n-methyl piperidine, the α- and β-carbon atoms of which are joined through the group $-CH_2-CH(OH)-$, so that tropine can, upon the other hand, be viewed as an oxyhexahydrobenzene derivative. Ecgonine, the basic decomposition product of cocaïne, is a tropine carboxylic acid. These kinships will in a measure account for the similar actions of atropine and cocaïne. As ecgonine is not capable of forming a lactone, Einhorn assumes that its alcoholic hydroxyl is attached to the β-carbon atom, and this explains the formula given above for tropine.

The constitution of tropine follows further from its decomposition reactions. We are indebted mainly to Ladenburg and Merling for our knowledge of these:

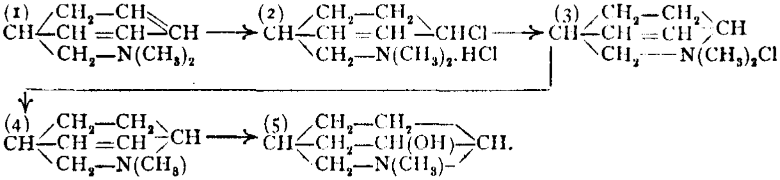
Decomposition of Tropine.—a. *Conversion of tropine into tropic acid, and into α-ethyl pyridine and picolinic acid:* Potassium permanganate oxidizes tropine (1) to tropigenine (2), whereas with chromic acid it first yields a ketone, tropinone (3), which upon reduction does not yield tropine again, but a ψ-tropine, which is always obtained by the decomposition of an alkaloid associated with cocaïne (p. 569) (B. **29**, 1636, 2228). When tropinone is further oxidized with chromic acid, tropic acid (4) results, which by proper decomposition is converted into normal adipic acid (B. **28**, 3271). Glacial acetic acid and hydrochloric acid split off water from tropine, and tropidine (5) results. The latter is oxidized by potassium permanganate to dihydroxytropidine (6). Further oxidation changes this body to tropic acid (4) (B. **28**, 2277). Zinc and hydrochloric acid reduce tropidine to hydrotropidine (7), a *saturated* compound, the chlorhydrate of which splits off methyl chloride in a current of hydrochloric acid gas, and becomes nordihydrotropidine (8). When the latter is distilled with zinc-dust, α-ethyl pyridine (9) is produced, which upon oxidation becomes picolinic acid (Ladenburg, B. **20**, 1647):

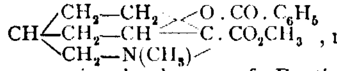


b. *The conversion of tropidine into benzyl bromide* (Merling, B. **24**, 3108; **26**, 1060). Tropidine (1) takes up methyl iodide, and, exposed to moist silver oxide, exchanges the iodine atom for hydroxyl, with the formation of tropidine methyl ammonium hydroxide (2), which is converted by boiling water into α-methyl tropidine or $\Delta_{5,5}$-dihydrobenzyldimethylamine (3). α-Methyl tropidine adds methyl iodide and acts further like the preceding body, with the production of α-methyl tropidine methyl ammonium hydroxide (4), which boiling water changes to tropilidene (5). The latter takes up two bromine atoms; its dibromide (6), heated to 100°, breaks down into HBr and benzyl bromide (7). Einhorn and Willstätter (A. **280**, 96) view tropilidene as a dihydrobenzene, in which two C-atoms holding the p-position are linked by the CH_2-group, similar to what we have, according to Bredt, in camphor. Consult B. **29**, 402, 490; **30**, 721, for analogous decompositions of tropinone and dihydrotropidine.



Synthesis of Tropine.—α-Methyl tropidine or $\Delta_{3,5}$-dihydrobenzyldimethylamine (1) forms a dihydrochloride: hydrochlor-α-methyl tropidine chlorhydrate (2). Sodium hydroxide splits off hydrochloric acid from this and there remains tropidine methyl ammonium chloride (3). By distillation the latter changes to tropidine (4), which takes up water on boiling with caustic alkali and reverts to tropine:



l-Cocaïne,  , melting at 98°, is lævogyratory. It is present in the leaves of *Erythroxylon coca.* It is a very superior local anæsthetic, and is applied in the form of hydrochloride. When it is digested with hydrochloric acid it breaks down into ecgonine, benzoic acid, and methyl alcohol.

It yields benzoyl ecgonine and methyl alcohol when boiled with water.

Conversely, cocaïne can be again re-formed from ecgonine, from benzoyl ecgonine, and from benzoyl ecgonine ester by introducing benzoyl into ecgonine ester, or, better, by esterifying benzoyl ecgonine with methyl alcohol. In this way certain alkaloids—*e. g.*, *cinnamyl cocaïne*, *truxilline*, etc.—associated with cocaïne (B. **27**, 783 Anm.) become valuable technically. In their decomposition they yield ecgonine methyl ester and ecgonine (B. **22**, 2960, R. 953).

Truxillic Acids, $\begin{array}{l} C_6H_5 . CH - CH . CO_2H \\ \quad\;\; | \qquad\;\; | \\ C_6H_5 . CH - CH . CO_2H \end{array}$ and $\begin{array}{l} C_6H_5 - CH - CH - CO_2H \\ \qquad\quad\; | \qquad\; | \\ CO_2H - CH - CH - C_6H_5 \end{array}$ (?), polycinnamic acids, dicinnamic acids, and also "natural isocinnamic acid," were discovered by Liebermann in his study of the secondary alkaloids of cocaïne. By distillation they yield ordinary cinnamic acid. The *a-acid* melts at 274°; the *β-acid* at 206°. Acetic anhydride and sodium acetate convert the first into the anhydride (m. p. 191°) of *γ-truxillic acid*, melting at 228° (B. **22**, 126). When the *β-acid* is fused with caustic potash it changes to *δ-truxillic acid*, melting at 174°. Potassium permanganate oxidizes the *β*-acid to benzil (B. **22**, 2254)—a reaction which, together with the inability to take up bromine and the stability of *β*-truxillic acid toward cold potassium permanganate, argues for the constitutional formula given above (B. **27**, 1410).

d-Cocaïne, melting at 43–45°, occurs in small quantities in the mixed cocaïne bases (B. **23**, 926). It is obtained synthetically from d-ecgonine (B. **23**, 982). See B. **27**, 1874, 1880, for cocaïnes substituted in the benzoyl group.

Tropa-cocaïne, *Benzoyl-ψ-tropine*, $C_{15}H_{19}NO_2$, melting at 49°, and found in

small amounts in the coca alkaloids, breaks down into benzoic acid and **ψ-tropine**, melting at 108° and boiling at 241°. The latter appears to be a stereoisomeride of tropine, because it can also be prepared by the reduction of tropinone, and when oxidized reverts to the latter. Indeed, tropine can be directly rearranged to ψ-tropine by means of sodium amylate. Potassium permanganate oxidizes ψ-tropine to ψ-tropigenine, which, like tropigenine, yields nortropinone upon oxidation (B. **29**, 936, 1636, 2231).

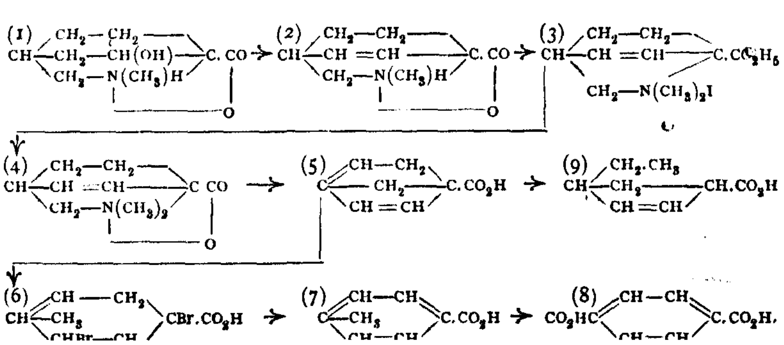
Mention may also be made here that crude cocaïne contains small quantities of **Hygrine**, $C_8H_{15}NO$, boiling at 92–94° (20 mm.). It is a derivative of n-methyl pyrrolidine, probably $\begin{matrix} CH_2CH{\diagup}COCH_2CH_3 \\ | \quad\quad > NCH_3 \\ CH_2CH_2 \end{matrix}$, as it forms an oxime, and when oxidized becomes *hygric acid*, or n-methyl pyrrolidine carboxylic acid, which parts with carbon dioxide very readily (B. **28**, 578) (p. 461).

l-Ecgonine, *Tropine Carboxylic Acid*, $CH{\begin{matrix} \diagup CH_2-CH_2 \text{———} \diagdown \\ -CH_2-CH(OH)- \\ \diagdown CH_2-NH(CH_3) \diagup \end{matrix}}C.CO$ (with O bridge) $+ H_2O$, melts at 205° when anhydrous. It is the basic decomposition product of l-cocaïne. When digested with caustic potash it changes to d-*ecgonine*, melting at 254°. See B. **24**, 7; **26**, 962, for the esters, amides, and nitriles of the ecgonines.

a-Ecgonine, $CH{\begin{matrix} \diagup CH_2-CH_2 \text{—} \diagdown \diagup COOH \\ -CH_2-C(OH) \\ \diagdown CH_2-N(CH_3) \diagup \diagdown CH \end{matrix}}$, melting at 305°, is a position isomeride of ecgonine. It has been prepared by adding hydrocyanic acid to tropinone (p. 568) and then saponifying the cyanhydrin (B. **29**, 2216).

Anhydroecgonine (see below), melting at 234°, is produced on boiling ecgonine hydrochloride with phosphorus oxychloride (B. **20**, 1221). The connection or relation of ecgonine to tropine follows as a consequence of the rearrangement of anhydroecgonine (observed by Einhorn), upon heating with hydrochloric acid to 280°, into tropidine, carbon dioxide being eliminated (B. **23**, 1338).

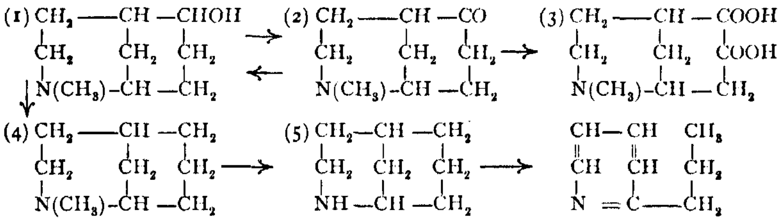
Decomposition of Ecgonine: The conversion of anhydroecgonine into p-toluic acid and terephthalic acid gives a clue as to the position of the carboxyl group in the tropidine ring of anhydroecgonine and also in ecgonine (B. **27**, 2439). If the anhydroecgonine (2) obtained by treating ecgonine hydrochloride (1) with $POCl_3$ be acted upon with methyl iodide after its conversion into the ethyl ester, anhydroecgonine ethyl ester iodmethylate (3) will be produced, and moist silver oxide will change it to anhydroecgonine methyl betaïne (4). Boiling alkalies convert the latter into dimethylamine and **p-methylene dihydrobenzoic acid** (5), melting at 33°. Its amide melts at 125°. By the addition of 2HBr p-methylene dihydrobenzoic acid becomes p-toluic acid dihydrobromide (6), which boiling sodium hydroxide changes to p-toluic acid (7), and terephthalic acid (8) is its oxidation product. The reduction of p-methylene benzoic acid produces $\Gamma a\Delta_2$-4-**ethylcyclopentene Carboxylic Acid** (9), boiling at 250–253°. Its *amide* melts at 158°.



If the preceding formula is correct, then p-methylene dihydrobenzoic acid would have as basis a ring-system similar to that observed with camphor (A. **280**, 96; B. **27**, 2439). **Hydroecgonidine**, $C_9H_{15}NO_2$, melting at 200°, is a saturated body. It is formed in the reduction of anhydroecgonine, and it can be decomposed like the latter. Here, however, the intermediate product, lacking above, between (4) and (5) can be fixed. It is a **tetrahydrodimethylbenzylamine p carboxylic ester**, the iodmethylate of which yields **tetrahydromethylene benzoic acid** when decomposed with alkali (B. **30**, 702).

Pelletierine, $C_9H_{15}NO$, **iso-**, **methyl-**, and **pseudopelletierine** (named after the chemist Pelletier), was discovered by Tauret in *Punica granatum*. Pseudopelletierine alone has been closely studied by Ciamician and Silber. They recognized this base as a near relative of the tropine series.

Pseudopelletierine, $C_9H_{15}NO$ (2), melting at 48° and boiling at 246°, corresponds to tropinone (p 568). By reduction it yields the alcohol corresponding to tropine: **methyl granatoline** (1), which chromic acid again converts into pseudopelletierine and subsequently oxidizes to *methyl granatic acid* (3), corresponding to tropic acid, whereas potassium permanganate splits off the methyl group and forms *granatoline*, analogous to tropigenine (p. 568). Hydriodic acid and phosphorus reduce methyl granatoline to *methyl granatine* (4) and *granatine* (5); the latter, distilled with zinc-dust, yields *a-propyl pyridine* (6):



When pseudopelletierine is decomposed with methyl iodide and alkali it is changed into a dihydroacetophenone analogous to dihydrobenzaldehyde. It, therefore, conducts itself like a ring homologue of tropinone (B. **29**, 481, 2972).

III. QUINOLINE GROUP OF THE ALKALOIDS.

Quina-bases.—The *quina-barks* (cortex chinæ) are derived chiefly from the various Cinchona species: *Cinchona Calisaya*, *C. lancifolia*, *C. Pitayensis*, etc.; also from the *Rubiaceæ*. They contain, in addition to tannin and *quinic acid* (p. 301), a series of bases, the most important of which are:

Quinine, $C_{20}H_{24}N_2O_2$,	Conquinine, $C_{20}H_{24}N_2O_2$,
Cinchonine, $C_{19}H_{22}N_2O$,	Cinchonidine, $C_{19}H_{22}N_2O$.

Quinine, $CH_3O.C_9H_5N.C_9H_{12}(OH)(CH_3)N$ (?) + $3H_2O$, melts, when anhydrous, at 177°. It consists of silky needles when crystallized from alcohol and ether. Pelletier and Caventou discovered quinine in 1820. It is one of our most valued medicines, especially for intermittent fevers, —*e. g.*, malaria, etc.,—and is an antidote for many infections produced by micro-organisms. *

* "Grundzüge der Arzneimittellehre," von C. Binz, 12. Aufl., 1894.

It is found (2–3 per cent.) in the yellow calisaya bark. It reacts alkaline, tastes bitter, and being a diacid base, forms primary and secondary salts.

The neutral *sulphate*, $(C_{20}H_{24}N_2O_2)H_2SO_4 + 8H_2O$, and the primary *hydrochloride*, $C_{20}H_{24}N_2O_2 . HCl + 2H_2O$, are employed in medicine. The former consists of long, shining needles, which fall to a white powder on exposure. It dissolves readily in dilute sulphuric acid, the solution exhibiting a beautiful blue fluorescence.

When chlorine water and then ammonia are added to the solution of quinine salt, there is produced a green precipitate, dissolving in an excess of ammonium hydroxide with an emerald-green color. On adding an alcoholic iodine solution to the sulphate in acetic acid, a *periodide*, $4Qu . 3SO_4H_2 . 2HI . I_4 + 6H_2O$, called *herapathite*, is precipitated. This crystallizes in emerald-green plates with golden lustre, and polarizes light the same as tourmaline.

Quinine is a tertiary diamine, and with metallic iodides yields the iodides, $C_{20}H_{24}N_2O_2 . CH_3I$ and $C_{20}H_{24}N_2O_2 . 2CH_3I$. The first of these yields the so-called methyl quinine, $C_{20}H_{23}(CH_3)N_2O_2$, when it is boiled with caustic potash. See B. **26**, 1968, for the ethyl iodide derivatives.

Cinchonine, $C_9H_6N . C_9H_{12}(OH)(CH_3)N$, is associated with quinine and occurs principally in the gray quinia bark (*Cinchona Huanaco*) (upward of 2.5 per cent.). It crystallizes from alcohol in white prisms, sublimes in needles in a current of hydrogen, and melts at 255°. Like quinine, it seems to dissipate fever, but to a less degree. Cinchonine is converted by boiling amyl alcoholic potash into cinchonidine (m. p. 201°), which is probably a stereoisomeride (B. **29**, 2185).

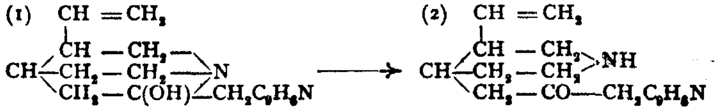
Quinine and cinchonine are similarly constructed; they contain one hydroxyl, and the former an additional methoxyl group. It is, therefore, methoxycinchonine:

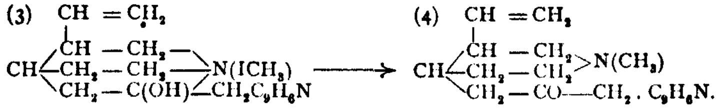
$C_{19}H_{21}(OH)N_2$	$C_{19}H_{20}(O.CH_3)(OH)N_2$
Cinchonine	Quinine.

They yield acetyl derivatives when heated with acetic anhydride. Quinine heated to 150° with hydrochloric acid splits off the methyl group, with formation of *apoquinine*, $C_{19}H_{20}(OH)_2N_2$. The two nitrogen atoms of both alkaloids are tertiary.

Decomposition of Cinchonine and Quinine: When cinchonine (1) and quinine are boiled with acetic acid, the union of that carbon atom to which hydroxyl is attached is severed from the one nitrogen atom, which then becomes an imido-group, while the C(OH)-group becomes a keto-group. Cinchonine yields the isomeric *quinchotoxine* (2), melting at 58–60°, which, like the corresponding *quinotoxine*, is very poisonous, but does not have any antipyretic properties. Quinchotoxine forms a methyl derivative (4), the iodmethylate of which appears to be identical with that of methyl cinchonine. The latter has been prepared by adding methyl iodide to cinchonine (3) and splitting off hydriodic acid (B. 13, 2292).

These observations have led v. Miller and Rhode (B. **28**, 1056) to regard cinchonine, which contains a quinoline ring, as a compound of quinoline with a piperidine ring, effected through a CH_2-group. The N-atom of the piperidine ring is linked through the group C(OH), to which the CH_2-group is attached, with the γ-carbon atom of the piperidine ring. The formulas recall those of tropine and ecgonine (p. 568):





The following of the many other decomposition reactions of cinchonine and quinine may be considered:

Oxidation of Cinchonine and Quinine: Potassium permanganate oxidizes cinchonine to cinchotenine, $C_{18}H_{20}N_2O_3 + 3H_2O$, melting at 197°. This is an oxycarboxylic acid, which can be as readily decomposed into a keton-imide as cinchonine itself. When cinchotenine is formed, formic acid appears, and a vinyl group probably becomes a carboxyl group. This would seem to be indicated by the addition of two bromine atoms, one molecule of hydrogen chloride, or HI to cinchonine (B. **19**, 2856). Cinchonine and quinine, when more energetically oxidized with potassium permanganate, yield cinchoninic acid, quinic acid, and eventually *α,β,γ-pyridine tricarboxylic acid*, or *carbocinchomeronic acid* (p. 536). It follows from this that cinchonine and quinone are γ-quinoline derivatives. When oxidized with chromic acid and dilute sulphuric acid, cinchonine (1) and cinchotenine yield, in addition to cinchoninic acid (3), *cincholoiponic acid* (5) (λοιπός, "remaining"), $C_8H_{13}NO_4 + H_2O$, melting at 125–127° with decomposition. This is probably a hexahydrohomocinchomeronic acid, $C_5H_9N(CH_2COOH)(COOH)$ (B. **28**, 12; **29**, R. 843; **30**, 1326). Cincholoiponic acid (5) is also found, when chromic acid is the oxidant, among the oxidation products of quinine (2) along with *quinic acid*, which is a methoxy-γ-quinoline carboxylic acid (4).

(1) $C_9H_6N.C_{10}H_{15}(OH)N$ ——	→ (3) $C_9H_6N.CO_2H$ . . .	γ-Quinoline Carboxylic Acid, Cinchoninic Acid.
	→ (5) $C_6H_{11}N(CO_2H)_2$ . .	Cincholoiponic Acid.
(2) $CH_3O.C_9H_5NC_{10}H_{15}(OH)N$ ——	→ (4) $(CH_3O)C_9H_5NCO_2H$	Methoxy-γ-quinoline Carboxylic Acid, Quinic Acid.

On the other hand, cinchonine is broken down by a chromic acid mixture into cinchoninic acid and *meroquinene* (from μέρος, "part"). The latter also results from a hydrolytic decomposition of cinquene and quinene, brought about by phosphoric acid at 170–180°. Lepidine or γ-methyl quinoline and p-methoxylepidine are produced at the same time. Meroquinene is converted into β-ethyl-γ-methyl pyridine on heating with corrosive sublimate and hydrochloric acid. When oxidized it becomes cincholoiponic acid. It probably should be regarded as β-vinyl-γ-piperidine acetic acid (B. **30**, 1326).

Lepidine and methoxylepidine are also formed in the alkali fusion of cinchonine and quinine (B. **23**, 2675).

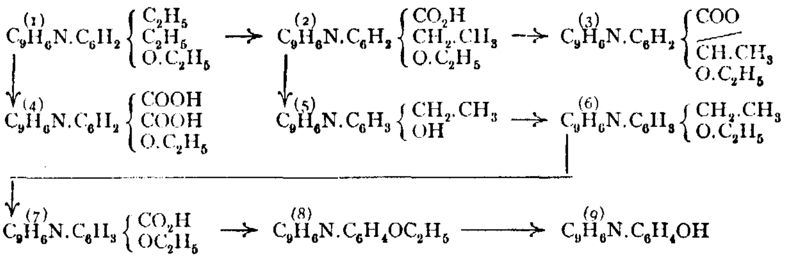
Decomposition of Cinchonine and Quinine Chlorides: PCl_5 converts cinchonine and quinine into *cinchonine* and *quinine chlorides*, and these compounds, boiled with alcoholic potash, yield *cinchene* and *quinene*, which, when heated to 190° together with concentrated hydrochloric or hydrobromic acid, give up ammonia and absorb water, thus forming *apocinchene* and *apoquinene*:

$C_9H_6N.C_{10}H_{15}(OH)N$	Cinchonine	$(CH_3O)C_9H_5N.C_{10}H_{15}(OH)N$	Quinine
↓ $C_9H_6N.C_{10}H_{15}ClN$ . .	" Chloride	$(CH_3O)C_9H_5N.C_{10}H_{15}ClN$.	Quinine Chloride
↓ $C_9H_6N.C_{10}H_{14}N$ . . .	Cinchene	$(CH_3O)C_9H_5N.C_{10}H_{14}N$ . .	Quinene
↓ $C_9H_6N.C_{10}H_{13}O$ . . .	Apocinchene	$(CH_3O)C_9H_5N.C_{10}H_{13}O$ . .	Apoquinene.

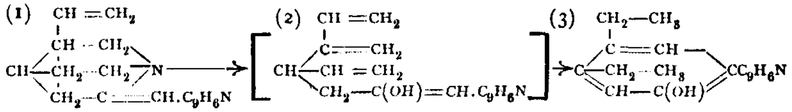
When apoquinene is heated to 250° with zinc-ammonium chloride it becomes amido-apocinchene, from which apocinchene may be obtained through the diazo-compound. As cinchonidine and conquinine can also be changed to cinchene and quinine, the four quinia-alkaloids (Königs, B. **27**, 903), cinchonine, quinine, cinchonidine, and conqui-

nine, are derived from cinchene. On the other hand, when the chlorides of the four alkaloids are reduced and the chlorine atoms replaced by hydrogen, four different desoxy-compounds result: *desoxycinchonine*, *desoxycinchonidine*, *desoxyquinine*, and *desoxyconquinine*. The isomerism of the two pairs of alkaloids appears, therefore, to be occasioned by the asymmetry of the tertiary carbon atom to which hydroxyl is attached.

Decomposition of Apocinchene into γ-o-Oxyphenyl Quinoline: Apocinchene is a phenol. Its ethyl ether (1) can be gradually oxidized to *ethyl apocinchenic acid* (2), the lactone of *ethyl apocinchene oxy-acid* (3), and *quinoline phenetol-dicarboxylic acid* (4), which forms an inner anhydride very readily, and consequently contains the CO_2H-groups in the o-position. Boiling concentrated hydrobromic acid decomposes ethyl apocinchenic acid into *homoapocinchene* (5), carbon dioxide and ethyl bromide being split off. Sulphuric acid and manganese dioxide oxidize *ethyl homoapocinchene* (6) to *ethyl homoapocinchenic acid* (7). If the silver salt of the latter be heated, *γ-quinoline phenetol* (8) is formed, which is converted by hydrobromic acid into *γ-quinoline phenol* (9). Apocinchene is, therefore, very probably **γ,2-oxy-4,5-diethylphenyl quinoline**, and apoquinene accordingly **γ,2-oxy-4,5-diethylphenylmethoxyquinoline.**

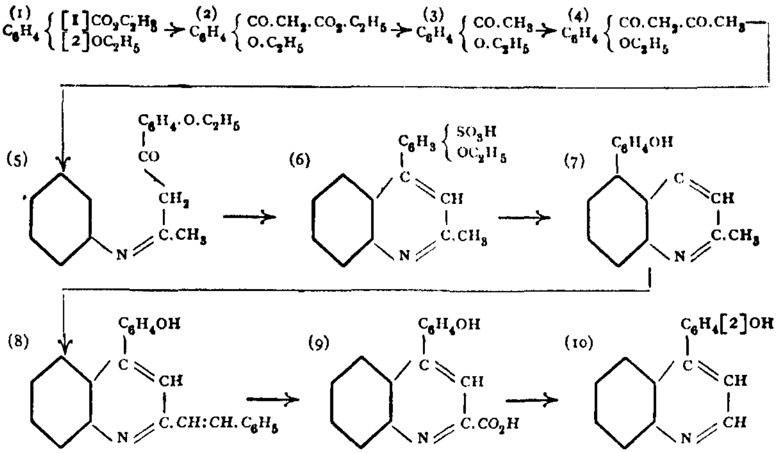


The following diagram represents the formation of γ,o-oxydiethylphenylquinoline, or apocinchene (3), by the hydrolysis of cinchene (1), assuming the formula (p. 573) given above for cinchonine:



The rearrangement of the hypothetical intermediate product (2) into the phenylquinoline derivative finds an analogy in the transpositions of the olefine terpenes (p. 309) into hydroaromatic compounds—*e. g.*, the production of isopulegole from citronellal (p. 308). It is probable that the breaking down of methyl cinchonine (p. 573) with methyl iodide and alkali would afford a better insight into the nature of the intermediate product (see A. 277, 277).

The **synthesis of γ,o-Oxyphenylquinoline** is identical with that of *γ-quinoline phenol* from apocinchene. It presupposes that of salicylic acid. The *diethyl ester of salicylic acid* (1), *acetic ester*, and sodium form o-*ethoxybenzoylacetic ester* (2), which is converted by boiling dilute sulphuric acid into o-*ethoxyacetophenone* (3). Acetic ester and sodium ethylate transpose the latter compound into o-*ethoxybenzoyl acetone* (4), from which o-ethoxybenzoylacetone-mono-anil (5) is obtained by digesting it with acetic acid and aniline. This anil condenses to *γ,o-ethoxyphenylsulphonic acid quinaldine* (6) on treating it with concentrated sulphuric acid. If the sulpho-acid be boiled with concentrated hydrobromic acid, *γ,o-oxyphenylquinaldine* (7) will result, and potassium permanganate will oxidize its *benzylidene compound* (8) to *γ,o-oxyphenylquinaldic acid* (9). The latter decomposes at 250° into carbon dioxide and **γ,o-oxyphenylquinoline** (10), identical with the γ-phenylquinoline prepared from apocinchene (Besthorn and Jaeglé, B. 27, 3035):



Strychnos Bases.—In the fruit of the different strychnos, principally in that of *Strychnos nux vomica* and in St. Ignatius' bean (*Strychnos Ignatii*), are found two very poisonous bases: *Strychnine* and *brucine*. Their constitution is undetermined. They were discovered (1818 and 1819) by Pelletier and Caventou.

Strychnine, $C_{21}H_{22}N_2O_2$, melting at 284° and boiling at 270° (5 mm.) (B. **19**, R. 30), is lævorotatory, reacts alkaline, has an extremely bitter taste, and occasions tetanus. Its most closely allied transposition products indicate that the one nitrogen atom belongs to a hydrogenized quinoline or indol ring and that it has sacrificed its basic character by union with a CO-group. Gradual oxidation with dilute and concentrated sulphuric acid converts strychnine into picric acid and an acid, $C_{10}H_5N_8O_8$, which splits off CO_2 when heated with water and very probably yields a **dinitrodioxyquinoline**, $C_9H_3N(NO_2)_2(OH)_2$ (Tafel, B. **26**, 333).

Brucine, $C_{23}H_{26}N_2O_4 + 4H_2O$, melts at 178° when anhydrous. It is lævorotatory. Its action is similar to that of strychnine, but less powerful. When fused with caustic potash it yields, in addition to lutidines and collidines, tetrahydroquinoline (B. **18**, R. 73; **20**, 460, 813).

It dissolves with a red color in concentrated nitric acid. On application of heat it becomes yellow and violet after the addition of stannous chloride.

The *veratrum alkaloids* occur, together with veratric acid (p. 228), in the white hellebore (from *V. album*) and in the sabadilla seeds (from *V. Sabadilla*). **Crystalline Veratrine** (B. **26**, R. 284), or **cevadine**, $C_{32}H_{49}NO_9$, melts at 202°. It dissolves in concentrated sulphuric acid with a yellow color, which gradually changes to blood-red. It yields β-picoline (B. **23**, 2707) by dry distillation.

IV. THE ISOQUINOLINE GROUP OF THE ALKALOIDS.

Opium Bases.—In opium, the dried juice of the green seed capsules of poppy (*Papaver somniferum*), we find not only meconic acid and meconine (p. 235), but a series of bases, of which may be mentioned:

Morphine, $C_{17}H_{19}NO_3$ (9 per cent.)	Papaverine, $C_{20}H_{21}NO_4$ (0.8 per cent.)
Codeïne, $C_{18}H_{21}NO_3$ (0.3 per cent.)	Narcotine, $C_{22}H_{23}NO_7$ (5 per cent.)
Thebaïne, $C_{19}H_{21}NO_3$ (0.4 per cent.)	Narceïne, $C_{23}H_{27}NO_8$ (0.2 per cent.).

The constitution of *papaverine, narcotine*, and *narceïne* remains unexplained. The nature of morphine, the principal base of opium, and its associates, codeïne and thebaïne, is not certainly known. They are very

probably not isoquinoline bodies, but are treated, however, with the other opium bases. Morphine is the most important of them from a medical point of view.

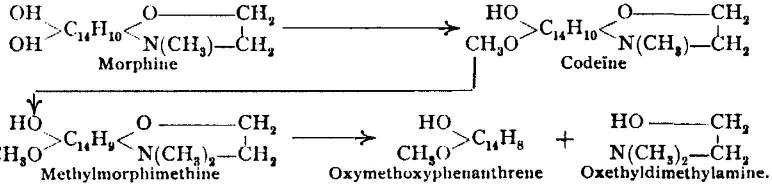
Morphine, $C_{17}H_{19}NO_3 + H_2O$, crystallizes from alcohol in small prisms, tastes bitter, and in small quantities produces sleep. It shows an alkaline reaction, and represents a tertiary, monacid base. Its officinal hydrochloride, $C_{17}H_{19}NO_3HCl + 3H_2O$, forms delicate, silky needles. It is used to relieve pain and to produce sleep.

The solutions of morphine and its salts are colored dark blue by ferric chloride; the solution in concentrated sulphuric acid acquires a blood-red coloration on the addition of a little nitric acid. It is readily oxidized, two molecules uniting, with the exit of two hydrogen atoms, to **pseudomorphine,** $(C_{17}H_{18}NO_3)_2$ (A. 294, 206). It contains two hydroxyl groups, and deports itself as a dihydric phenol, forming salts with one metal atom, but yielding diacidyl derivatives. It forms phenanthrene on distillation with zinc-dust.

Apomorphine, $C_{17}H_{17}NO_2$, results when water is split off from morphine by heating the latter with concentrated hydrochloric acid to 140–150°. Its hydrochloride is applied in the liberation of mucus.

Codeïne, Methyl Morphine, $C_{17}H_{17}\begin{pmatrix}OH \\ O.CH_3\end{pmatrix}NO$, melting at 150°, is contained in opium, and is obtained from morphine by means of methyl iodide and potassium hydroxide (B. 14, 1413).

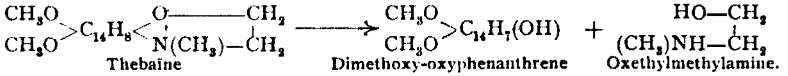
Codeïne iodmethylate, which is also produced from morphine methyl hydroxide (Const. B. 30, 354) and methyl iodide, yields, upon heating with alkali, the so-called **methylmorphimethine,** melting at 118°. When this is digested with acetic anhydride it is resolved into acetoxymethoxyphenanthrene and acetoxyethyldimethylamine (B. 26, R. 494; 27, 1144):



Apocodeïne is obtained, like apomorphine, from morphine.

Thebaïne, $C_{19}H_{21}NO_3 = C_{17}H_{15}(OCH_3)_2NO$, consists of silvery plates, melting at 193°. It breaks down into $2CH_3Cl$ and **morphothebaïne,** when heated with concentrated hydrochloric acid. This new isomeric base melts at 191° (B. 27, 2961).

Thebaïne or its iodmethylate is decomposed, like codeïne, on boiling with acetic anhydride, into acetylthebaol, an acetoxydimethoxyphenanthrene and oxethylmethylamine:

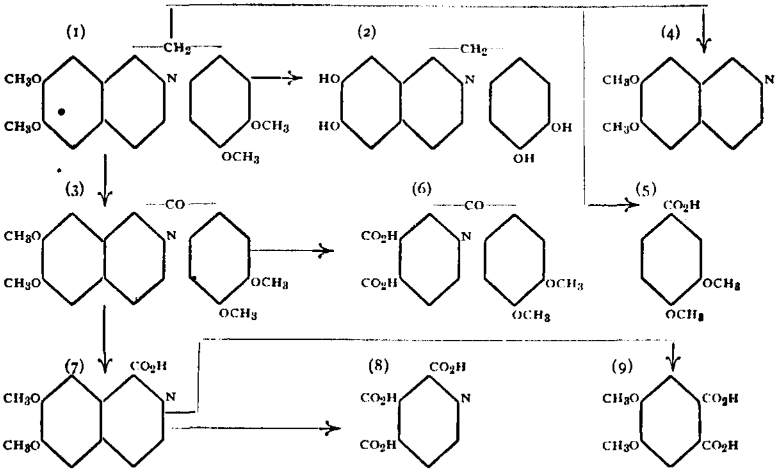


Boiling dilute hydrochloric acid changes thebaïne, a tertiary base, into the secondary base **Thebenine,** $C_{17}H_{16}(OH)(OCH_3)NO$. When this is treated with ethyl iodide and decomposed with caustic potash, methyldiethylamine and **thebenol,** $C_{16}H_{10}(OCH_3)(OH)$, result. *Pyrene* (p. 420) (B. 30, 1357) is produced in the distillation of thebenol with zinc-dust.

Papaverine (1), *Tetramethoxybenzylisoquinoline,* $C_{20}H_{21}NO_4$, melts at 148°. Its constitution becomes evident from its decompositions. Hot hydriodic acid decomposes it into $4CH_3I$ and the base *papaveroline* (2). Potassium permanganate oxidizes it to *papaveraldine* (3), or tetramethoxybenzoylisoquinoline.

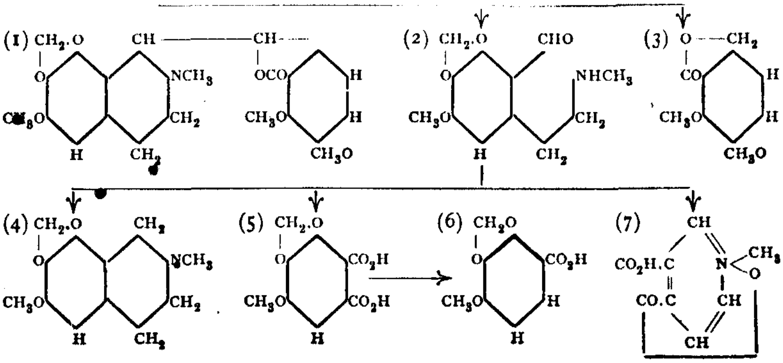
Papaverine breaks down into veratric acid (5) and dimethylisoquinoline (4) when fused with caustic potash.

The oxidation of papaveraldine gives rise to papaveric acid, α-dimethoxylbenzoyl-pyridine-β,γ-dicarboxylic acid (6), *dimethoxyisoquinoline carboxylic acid* (7), *α,β,γ-pyridinitricarboxylic acid* (8), and *metahemipinic acid* (9) (G. Goldschmidt, B. **21**, R. 650). Compare the following diagram. The hydrogen atoms are omitted from the rings in order that the representation may be clear:



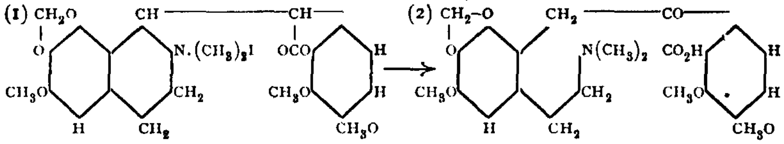
Narcotine (1), *Meconinehydrocotarnine*, $C_{22}H_{23}NO_7$, melting at 176°, is separated from morphine by potassium hydroxide, in which it is insoluble (1817, Robiquet). Boiling water decomposes it into cotarnine (2), melting at 132° (1844, Wöhler, A. **50**, 1), an amidoaldehyde and meconine (p. 235) (3). The latter yields opianic acid (p. 237) and hemipinic acid (p. 242) on oxidation.

Cotarnine is an aldehyde. It forms salts with acids, water being eliminated and the isoquinoline ring being closed. Cotarnine upon reduction becomes hydrocotarnine (4), while potassium permanganate oxidizes it to cotarnic acid (5), a methylmethylenetrioxybenzene dicarboxylic acid, which yields methylmethylenegallic acid (6) on being heated with hydrochloric acid, and gallic acid with hydriodic acid (W. Roser, A. **249**, 156; **254**, 334; **272**, 221). Nitric acid oxidizes cotarnine to apophyllenic acid (7) (see B. **29**, 2190). It must be observed that the position assumed, in the following formulas, for the dioxymethylene and methoxy-groups in the isoquinoline nucleus is wholly arbitrary:

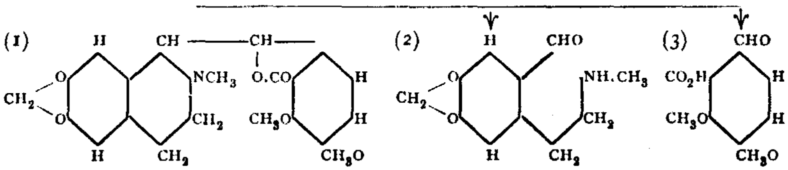


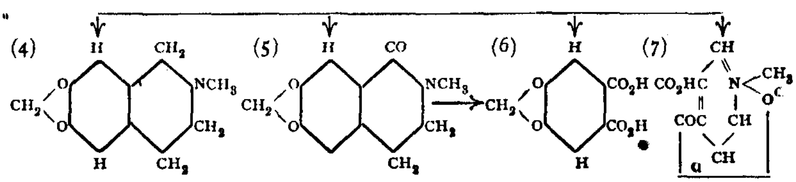
In the attempt to prepare narcotine by condensing opianic acid and hydrocotarnine with sulphuric acid an isomeric **isonarcotine**, melting at 194°, resulted. It may be recognized by the red coloration it gives with concentrated H_2SO_4 (B. 29, 183, 2040).

Narceïne (2), $C_{23}H_{27}NO_8 + 3H_2O$, melting at 170°, and when anhydrous at 140–145°, occurs, together with narcotine, in opium, and is formed when the iodmethylate (1) of narcotine is acted upon with caustic potash (A. 286, 248):

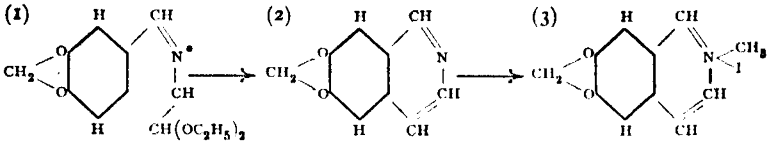


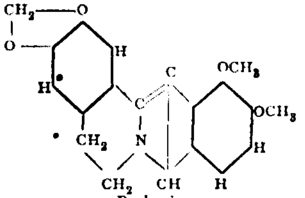
Hydrastine (1), $C_{21}H_{21}NO_6$, melting at 132°, $[\alpha]_D = -67°$ in chloroform (1851, Durand), occurs, together with **berberine**, $C_{20}H_{17}NO_4 + 5\frac{1}{2}H_2O$, melting at 120° (it is found with hydrastine in *Berberis vulgaris*), in the roots of *Hydrastis canadensis*, a North American plant belonging to the Ranunculaceæ. It is constituted similarly to narcotine. When acted upon by oxidizing agents it breaks down into opianic acid (3) (p. 237) and **hydrastinine** (2), melting at 116°, which carries the hydrastine. Hydrastine, like cotarnine, is an aldehyde. Reducing agents convert it into the corresponding alcohol, which at once loses water and becomes hydrohydrastine (4), Bz-2,3-methylenedioxy-tetrahydroisoquinoline. Potassium permanganate oxidizes hydrastinine first to oxyhydrastinine (5), then to hydrastininic acid, which nitric acid converts into the methyl imide of hydrastic acid (6) or normetahemipine methylene ether acid. Hydrastinine itself, like cotarnine, is oxidized by nitric acid to apophyllenic acid (6). The isoquinoline ring is present in the salts of cotarnine and hydrastine. The formation of salts follows in consequence of the exit of water (W. Roser, A. 249, 172; Freund, A. 271, 311):





The synthesis of hydrastinine was effected in the following manner: **Piperonal-acetalamine** (1) condenses with sulphuric acid to Bz-2,3-**methylenedioxyisoquinoline**, melting at 124° and boiling at 215° (50 mm.), which becomes **hydrohydrastinine** (see above), melting at 60–61°, upon reducing its iodmethylate (3), melting at 244°, with tin and hydrochloric acid. Potassium bichromate and sulphuric acid change the hydro-derivative back to hydrastinine (Fritsch, A. 286, 18):





Berberine.

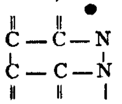
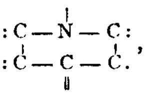
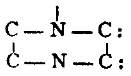
Berberine is even more complex in its constitution than hydrastine. The constitutional formula, here presented, has been deduced from its decomposition reactions (Perkin, Jr., B. **24**, R. 157). The position of the dioxymethylene group in this formula is based upon the synthesis of oxyhydrastinine from the decomposition products of berberine. The constitution of oxyhydrastinine has been determined by its conversion into hydrastic acid.

B. POLYHETERO-ATOMIC SIX-MEMBERED RINGS.

AZINES.

Polyhetero-atomic six-membered rings, containing oxygen and sulphur as ring members, occur in a series of bodies which have already been discussed at the conclusion of allied bodies. Dialkylen ethers—*e.g.*, *diethylene oxide* (I, 298)—and the anhydrides of α-oxyacids—*e. g.*, *glycollide*, *diglycollic anhydride* (I, 339)—contain rings consisting of four carbon atoms and two oxygen atoms. The six-membered ring of *diethylene disulphide* (I, 305), and of thianthrene or diphenylene disulphide (II, 518), contains two sulphur atoms, while three oxygen atoms or three sulphur atoms are present in the polymeric aldehydes and the thioaldehydes—*e. g.*, *trioxymethylene*, *trithiomethylene*, *paraldehyde*, *trithioaldehyde* (I, 194, 203), etc. (see II, 441).

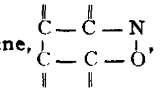
Those members of this division containing N-atoms as ring members require more exhaustive consideration. This was done also with like bodies of the five-membered series. They may be regarded, like the azoles, as derived from furfurane, thiophene, and pyrrol by the replacement of methine groups of monoheteroatomic rings, and accordingly they can be grouped under the common name of *azines*.

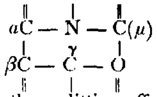
The *oxazines*, *oxdiazines* (azoxazines), and *dioxdiazines* are then the rings with the hetero-atoms: N and O, 2N and O, 2N and 2O; the *thiazines* and *thiodiazines* (diazthines) are the rings with the hetero-atoms S and N, S and 2N, and the *diazines*, *triazines*, and *tetrazines* are the six-membered rings with 2, 3, and 4 N-atoms. The place isomerides of diheteroatomic azines are distinguished according to the position of the hetero-atoms with reference to one another by the prefixes ortho-, meta-, and para-. Thus, the three possible diazines as ***orthodiazine***, , ***metadiazine***, , and ***paradiazine***, 

(B. **22**, 2083; A. **249**, 1; J. pr. Ch. **38**, 185); the oxazines as ***orthoxazines***, ***metoxazines***, ***paroxazines***; the thiazines as ***orthothiazines***, ***metathiazines***, and ***parathiazines***.

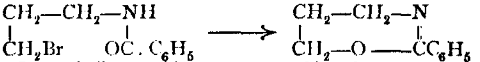
The parent substances of important classes of dyes: compare *resorufin*, *methylene blue*, *toluylene red*, *safranines*, *indulines*, are the dibenzo-derivatives of the paroxazines, parathiazines, and paradiazines.

1. OXAZINES.

A. The ring of **orthoxazine**, , is present in the oxime anhydrides of the γ-aldehydo- and γ-ketonic acids—*e. g.*, benzal lævoxime, $C_6H_5CH:CH-CH_2-CO$ / $CH_3.C \text{———} N-O$ (p. 288), which bear the same relation to the oxime anhydrides of the β-ketonic acids, the isoxazolons (p. 495), as the δ-lactones to the γ-lactones (B. 25, 1930). The ring formation of the oximes of o-benzaldehyde and o-benzo-ketone carboxylic acids occurs without difficulty. Derivatives of *benzorthoxazines* are produced: **Benzorthoxazinon**, *o-Benzaldoxime carboxylic anhydride*, $C_6H_4\langle{}^{CH=N}_{CO-O}$, is derived from phthalaldehydic acid (p. 236). It readily rearranges itself to the isomeric phthalimide (B. 24, 2347). There is an intermediate formation of o-cyanbenzoic acid (see the indoxazenes, p. 495). **Benzomethylorthoxazinon**, *o-Acetophenonoxime carboxylic anhydride*, $C_6H_4\langle{}^{C(CH_3)=N}_{CO\text{———}O}$, melts at 179° (B. 16, 1995, and p. 238).

B. The following contain the **Metoxazine ring**, :

I. The *pentoxazolines*, which are produced by the splitting-off of HBr from the γ-bromalkylamides. This is similar to the formation of the five-membered oxazolines (p. 503) from the β-bromalkylamides (B. 24, 3213):



γ-Bromethylbenzamide — μ-Phenylpentoxazoline.

μ-Phenyl-α-methyl Pentoxazoline, $C_4H_6NO(CH_3)(C_6H_5)$, and **μ-Phenyl-α-dimethyl-γ-methyl Pentoxazoline**, $C_4H_3NO(CH_3)_3(C_6H_5)$, melting at 32°, are obtained from γ-chlorbutyl- and γ-bromisohexylbenzamide.

μ-Allylamido- and μ-phenylamido-γ-methyl Pentoxazoline, or *n-allyl* and *n-phenyl butylene-ψ-urea*, $\begin{matrix} CH_2 \text{———} CH_2-N \\ CH(CH_3)-O \text{——} C(NHR) \end{matrix}$, are obtained from γ-chlorbutylamine by means of allyl- and phenyl-mustard oil (B. 29, 1428; 30, 1319).

II. Derivatives of *benzometoxazine* or *phenpentoxazoline* are formed from o-amidobenzylhalogenides (p. 180) and acid anhydrides (B. 27, 3515):

o-Amidobenzyl Bromide — μ-Methylphenpentoxazoline.

The *coumazonic acids* (p. 236 and B. 16, 2585) also belong here—*e. g.*, **μ-Methyl Coumazonic Acid**, *Benzotrimethylmetoxazine*, $C_6H_4\langle{}^{C(CH_3)_2-O}_{N\text{=====}C.CH_3}$, melting at 218°, and **μ-Phenyl Coumazonic Acid**, *Benzodimethyl-μ-phenylmetoxazine*, $C_6H_4\langle{}^{C(CH_3)_2-O}_{N\text{=====}C.C_6H_5}$, melting at 220°, which have been obtained from 3-amido-

4-oxypropylbenzoic acid with acetyl chloride and benzoyl chloride. Carbon dioxide is liberated.

The *imido-* and *thio-coumazones* are derivatives of *dihydrobenzometoxazine*. The former result upon the exit of water from the urea derivatives of o-amidobenzyl alcohol (p. 185), the latter by the action of CS_2 upon the alcoholic solution of o-amidobenzyl alcohol and related compounds:

$$C_6H_4\langle{}^{CH_2OH}_{NH.CO.NH.C_6H_5} \longrightarrow C_6H_4\langle{}^{CH_2O}_{NH.C:N.C_6H_5} \qquad C_6H_4\langle{}^{CH_2OH}_{NH_2} \xrightarrow{CS_2} C_6H_4\langle{}^{CH_2O}_{NH.CS}$$

Phenylimidocoumazone — Thiocoumazone.

The imido-coumazones are isomeric with the keto-tetrahydroquinazolines (p. 592), and when digested with aromatic amines become quinazoline compounds (p. 589). The O-member is replaced by NR. The thiocoumazones behave similarly (B. 27, 2424).

Phenylimidocoumazone, *Benzodihydrometoxazine anil*, $C_8H_7ON:(NC_6H_5)$, melting at 146° (B. 22, 2938), forms stable salts with acids; with acid anhydrides and chlorides it yields addition products. **Thiocoumazone, Benzodihydrothiometoxazine,** $C_8H_7ON:S$, melting at 142°, is an acid, and forms a sparingly soluble potassium salt (B. 25, 2979; 27, 1866).

C. **Paroxazines,** $\begin{matrix} N-C-C \\ | \qquad\quad | \\ C-C-O \end{matrix}$: I. Only saturated derivatives of the simple nucleus are known. The following are *tetrahydroparoxazines*: **Morpholine** (1, 310) and its alkylic compounds. n-**Benzyl Morpholine,** boiling at 261°, is produced from dibromethylbenzylamine, and also from chlorethylbenzylamine (B. 24, R. 821; 29, 2386). **Diglycollo-imide** and the derivatives of isomeric **diglycollamid-anhydride** (B. 25, 2272) are *diketotetrahydroparoxazines*:

$$O\langle{}^{CH_2-CH_2}_{CH_2-CH_2}\rangle NH \qquad O\langle{}^{CH_2-CO}_{CH_2-CO}\rangle NH \qquad O\langle{}^{CO-CH_2}_{CO-CH_2}\rangle NH$$

Morpholine — Diglycollo-imide — Diglycollamid-anhydride.

II. *Benzoparoxazine* yields: β-**Phenylbenzoparoxazine,** $C_6H_4\langle{}^{O\,-\,CH_2}_{N\,-\,C\,.\,C_6H_5}$, melting at 103°, and β-**methylbenzoparoxazine.** They are obtained by the reduction of o-nitrophenylphenacyl ether, $C_6H_4\langle{}^{O\,.\,CH_2\,.\,CO\,.\,C_6H_5}_{NO_2}$, and o-nitrophenacetal (B. 23, 172). **Benzomorpholine,** $C_6H_4\langle{}^{O\,-\,CH_2}_{NH\,-\,CH_2}$, boiling at 268°, is made from o-oxethylamidophenol (p. 152). **Benzoketomorpholine,** $C_6H_4\langle{}^{O\,-\,CO}_{NH\,-\,CH_2}$, is produced by reducing glycol-o-nitrophenyl ether acid, $C_6H_4(NO_2)OCH_2COOH$ (B. 20, 1943).

III. The group of *dibenzoparoxazine* or *phenoxazine*, *benzonaphtho-*, and *dinaphthoparoxazine* has been more fully developed. A series of important dyes belongs to it:

Phenoxazine, $C_6H_4\langle{}^{O}_{NH}\rangle C_6H_4$, melting at 148°, is produced on heating o-amidophenol with pyrocatechol (p. 160).

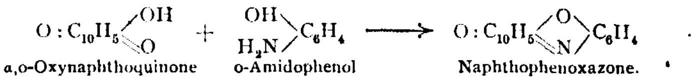
The dyes of the phenoxazine group contain quinone unions (p. 167). They may also be regarded as quinone anils, indophenols, or indamines (p. 174), in which the two nuclei are further united by an oxygen atom in the ortho-position with reference to the tertiary nitrogen:

$$O:C_6H_4=N-C_6H_4OH \qquad O:C_6H_3\langle{}^{N}_{O}\rangle C_6H_3OH$$

Indophenol — **Oxyphenoxazone (Resorufin).**

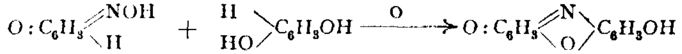
The parent bodies of the phenoxazine dyes are distinguished as *phenoxazones*, or *phenoxazines* (B. **25**, 2995), depending upon whether they are quinone-monimide or di-imide derivatives. They are produced:

1. Upon condensing o-oxyquinones and o-oxyquinone-imides with o-amidophenols. The oxy-p-quinones of the naphthalene series are mainly best adapted for these condensations (B. **26**, 2375; **28**, 353):



a,o-Oxynaphthoquinone o-Amidophenol Naphthophenoxazone.

2. Oxy- and amido-derivatives of the phenoxazones and phenoxazimes, the real dyes, result by the condensation of quinone dichlorimides, nitrosophenols, or nitrosodimethyl aniline with polyhydric phenols or tertiary amidophenols:



Nitrosophenol Resorcinol Oxyphenoxazone.

Resorufin, Oxyphenoxazone, $O:C_6H_3(NO)C_6H_3(OH)$, is produced when nitric acid containing N_2O_3 acts upon an ethereal solution of resorcinol (p. 160) (Weselsky, A. **162**, 273); and from nitrosoresorcinol by means of resorcinol (B. **24**, 3366). *Resazurine*, $O:C_6H_3\langle{}^{N—}_{(NO)}\rangle C_6H_3(OH)$, is an intermediate product in this reaction. The alkaline solutions of resorufin are rose-red, with a magnificent cinnabar-red fluorescence. **Orcirufin** is obtained, like resorufin, from orcinol (p. 162). **Gallocyanine,** *Dimethyl-amido-oxyphenoxazon-carboxylic acid*, $N(CH_3)_2 . C_6H_3(NO)C_6H(OH)COOH : O$, is produced by the action of nitrosodimethylaniline upon gallic acid (p. 230). With mordants, especially chromic oxide, it forms violet-colored and stable *lakes* (calico printing).

Chloroxydiphenoxazone, $C_6H_4(NO)C_6HCl(OH):O$, melting with decomposition at 235°, is obtained from p-dioxychlorquinone and amidophenol (B. **26**, 2375).

Naphthophenoxazone, $O=C_{10}H_5(NO)C_6H_4$, melts at 192°. **Naphthophenoxazine,** $NH:C_{10}H_5(NO)C_6H_4$, melting at 243°, is prepared from o-amidophenol and oxynaphthoquinone imide (p. 407).

Dimethyl Naphthophenoxazime Chloride, $C_{10}H_6(NO)C_6H_3:N(CH_3)_2Cl$, from β-naphthol and nitrosodimethyl aniline, is the so-called *naphthol blue*, which dyes cotton mordanted with tannin a violet-blue (B. **23**, 2247). *Nile blue* is an amido-derivative of naphthol blue, while *cyanamine* is an anilido-derivative. For other derivatives consult A. **289**, 90; B. **29**, R. 1000).

Oxyphenoxazime, $C_6H_4\langle{}^{N}_{O}\rangle C_6H_2\langle{}^{OH}_{NH}$, results from the oxidation of o-amidophenol. It condenses to **triphendioxazine,** $C_6H_4\langle{}^{N}_{O}\rangle C_6H_2\langle{}^{O}_{N}\rangle C_6H_4$, with another molecule of amidophenol (p. 153; B. **23**, 182; **27**, 2784). See B. **29**, 2076, for **methyl triphendioxazine.**

2. THIAZINES.

A. **Orthothiazines:**

C—C—N
C—C—S

, are not known.

B. **Metathiazine,**

(a)C—N—C(μ)
C—C—S
(β) (γ)

. The following bodies are derived from this ring:

I. The *penthiazolines*, corresponding to the pentoxazolines. They are prepared from the γ-haloid alkylthiobenzamides.

μ-Phenyl Penthiazoline, $\begin{matrix} CH_2 . CH_2 . N \\ | \qquad\qquad \| \\ CH_2 . S — C . C_6H_5 \end{matrix}$, melting at 45°, is obtained from thiobenzamide (p. 204) and trimethylene chlorbromide (B. **26**, 1077). **μ-Phenyl-α-dimethyl-γ-methyl Penthiazoline,** $C_4H_3NS(CH_3)_3(C_6H_5)$, melting at 34°, is derived from γ-bromisohexylthiobenzamide. **μ-Mercapto-γ-methyl Penthiazoline** and **-γ-methyl-α-dimethyl Penthiazoline,** melting at 131° and at 180°, are made from γ-chlorbutylamine and γ-bromisohexylamine by the action of carbon bisulphide (B. **29**, 1429; **30**, 1321; see also B. **29**, R. 648 and 684).

Diketopenthiazolidine, Sinapan-propionic Acid, $\begin{matrix} CH_2 — CO — NH \\ | \qquad\qquad | \\ CH_2 — S — CO \end{matrix}$, melting at 159°, results when β-iodpropionic acid acts upon xanthogenamide (B. **24**, 3848).

II. Derivatives of *benzometathiazine* or *phenpenthiazole* are produced in the interaction of o-amidobenzyl haloids and carbon-thiamides (pp. 180, 204) (B. **27**, 3519):

$$C_6H_4\begin{matrix} \diagup CH_2Br \\ \diagdown NH_2 \end{matrix} + NH_2CS . CH_3 \longrightarrow C_6H_4\begin{matrix} \diagup CH_2—S \\ \qquad\quad | \\ \diagdown N——C . CH_3 \end{matrix}.$$

μ-Methyl Phenpenthiazole, melting at 46°, is produced by the action of P_2S_5 upon μ-methyl phenpentoxazole; also from o-acetylamidobenzyl alcohol and P_2S_5, as well as from o-acetylamidobenzyl sulphide and PCl_5. Consult B. **30**, 1143, for other derivatives.

The *imido-* and *thio-coumothiazones*, corresponding to the imido- and thiocoumazones, belong here. Like them, they result from the action of CS_2 and alcoholic potash upon the thio-urea derivatives of o-amidobenzyl alcohol—or amidobenzyl alcohols in general (p. 180):

Thiocoumothiazone, *Benzodihydrothiothiazine,* $C_6H_4\begin{matrix} \diagup NH — CS \\ \qquad\quad | \\ \diagdown CH_2 — S \end{matrix}$, melting at 166°, is an acid. It forms n-phenylthiotetrahydroquinazoline when boiled with aniline, the ring sulphur atom being replaced by NC_6H_5 (pp. 581, 592). **Imido-coumothiazone,** *Benzylene-ψ-thiourea,* $C_6H_4\begin{matrix} \diagup NH — C : NH \\ \qquad\quad | \\ \diagdown CH_2 — S \end{matrix}$ or $C_6H_4\begin{matrix} \diagup N = C . NH_2 \\ \qquad\quad | \\ \diagdown CH_2 — S \end{matrix}$, melting at 137°, is produced in the reduction of o-nitrobenzyl sulphocyanide, as well as from o-amidobenzyl chloride and thiourea. Potassium permanganate oxidizes it to α-quinazolon, while digested with aniline it forms **phenylimido-coumothiazone,** *benzodihydrothiazine anil,* melting at 197°, which results upon expelling water from o-oxytolylphenylthiourea (B. **22**, 2933; **27**, 2429).

C. **Parathiazine,** $\begin{matrix} C — N — C \\ | \qquad\quad | \\ C — S — C \end{matrix}$: **Ketodihydrobenzothiazine,** $C_6H_4\begin{matrix} \diagup NH — CO \\ \qquad\quad | \\ \diagdown S —— CH_2 \end{matrix}$, is a benzo-derivative which may possibly originate from this ring. It melts at 179°, and is produced by the interaction of o-amidothiophenol and brom-acetic acid (B. **30**, 607).

The symmetrical dibenzo-derivatives—*e. g., dibenzo-* and *dinaphtho-parathiazine,* or *thiodiphenylamine* (p. 80), and *thiodinaphthylamine* (p. 396)—are more important. Thiodiphenylamine corresponds to phenoxazine or dibenzoparoxazine (p. 581), and, like the latter, is the parent substance of a series of more important dyes, among which is the very valuable methylene blue.

Thiodiphenylamine, $C_6H_4<\begin{matrix} S \\ NH \end{matrix}>C_6H_4$, melting at 150° and boiling at 370°, is prepared analogously to phenoxazine by heating o-amidothiophenol and pyrocatechol to 220°. An easier course consists in heating diphenylamine to 250° with sulphur or S_2Cl_2 (B **21**, 2063). It is a neutral body, the imide hydrogen of which can be replaced by alkyl and acid radicals. See B. **24**, 2910, for the *urea derivatives.* **Tetrachlor-**

thiodiphenylamine melts at 235° (B. **29**, 1363). Nitric acid oxidizes thiodiphenylamine to **nitrodiphenylamine sulphoxide,** $C_6H_4<{SO \atop NH}>C_6H_3NO_2$, which can be reduced to *amidothiodiphenylamine*. The reduction of *dinitrodiphenylsulphoxide* yields **Diamidothiodiphenylamine,** *Leucothionine*, $NH_2.C_6H_3<{S \atop NH}>C_6H_3NH_2$, which is produced on heating p_2-diamidodiphenylamine, $(NH_2C_6H_4)_2NH$, with sulphur. It is the leuco-base of the simplest thionine dye into which it can be converted by oxidation with ferric chloride. The *tetramethyl derivative* of leucothionine is the leuco-base of methylene blue (see below).

The dye-substances of the thiodiphenylamine group contain quinone unions. Like the paroxazine dyes, they are to be viewed as indophenol and indamine derivatives, in which the two phenyl groups are further united by sulphur:

$$NH_2.C_6H_4—N=C_6H_4:NH \xrightarrow{S} NH_2.C_6H_3\left\langle {N \atop S} \right\rangle C_6H_3=NH$$

Phenylene Blue (p. 174) Lauth's Violet.

The *phenthiazimes* and *phenthiazones*, like the phenoxazimes and phenoxazones, are distinguished according as they represent quinonediimide or monimide derivatives. Lauth's dye-substances belong to the phenthiazimes (Bernthsen, A. **230**, 73; **251**, 1). They result upon oxidizing paraphenylenediamines in the presence of hydrogen sulphide. It is probable that indamines occur as intermediate products (p. 174):

$$2NH_2C_6H_4NH_2 \xrightarrow[-5H]{+S} NH_2C_6H_3\left\langle {N \atop S} \right\rangle C_6H_3:NH.$$

Another procedure which may be adopted in the preparation of these dyestuffs is based upon the fact that indamines and thiosulphuric acid yield thiosulphonic acids, which change to the leuco-bases of the thiazine dyestuffs upon boiling them with dilute acids. Therefore, the dyestuffs can be obtained by oxidizing a mixture of one molecule of p-diamine with one molecule of a monamine, which form the indamine, in the presence of a thiosulphate. Thiazones are produced when p-amidophenols are oxidized in the presence of hydrogen sulphide.

Amidophenthiazine, Thionine, *Lauth's Violet*, $NH_2.C_6H_3(NS)C_6H_3:NH$, is obtained from p-phenylenediamine, and also from its leuco-base, diamidothiodiphenylamine, by oxidation.

Methylene Blue, *Tetramethylamidophenthiazimium chloride*, $(CH_3)_2N.C_6H_3(NS)C_6H_3:N(CH_3)_2Cl$ (Caro, 1877), results upon oxidizing two molecules of dimethyl-p-phenylenediamine in H_2S-solution, or one molecule of dimethyl-p-phenylenediamine with one molecule of dimethyl aniline and thiosulphate.

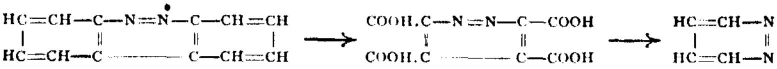
It dyes silk, or cotton mordanted with tannic acid, a beautiful *fast blue*.

Phenthiazone, $C_6H_4(SN)C_6H_3O$, results upon oxidizing oxythio-diphenylamine. **Oxyphenthiazone, Thionol,** $HO.C_6H_3(NS)C_6H_3:O$, is produced on boiling thionine with dilute acids or alkalies.

3. DIAZINES.

A. Orthodiazines, $\begin{matrix} (4) & (3) & \\ C — & C — & N\ (2) \\ | & | & \\ C — & C — & N\ (1) \\ (5) & (6) & \end{matrix}$: I. **Orthodiazine** or **'Pyridazine,** $C_4H_4N_2$,

melting at 8° and boiling at 208°, may be prepared from its tetracarboxylic acid, the oxidation product of dibenzorthodiamine or phenazone (p. 587):

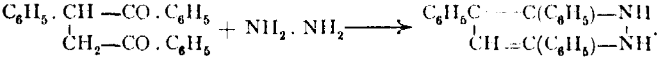


Phenazone — Pyridazine Tetracarboxylic Acid — Pyridazine.

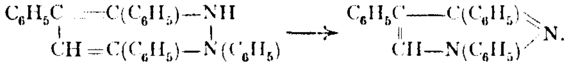
Pyridazine is an oil with an odor like that of pyridine. It forms very soluble salts, and addition compounds with $AuCl_3$, $HgCl_2$, etc. **Pyridazine Dicarboxylic Acid**, $C_4H_2N_2(CO_2H)_2$, melting with decomposition at 205°, is obtained from the dipotassium salt of the tetracarboxylic acid.

3,4,6-**Triphenyl Pyridazine**, $C_4H(C_6H_5)_3N_2$, melting at 171°, is readily produced by oxidizing its dihydro-derivative.

Dihydropyridazines are formed from the 1,4 diketones and hydrazines, either without or together with the n-amidopyrrols, which are to be expected:



3,4,6-**Triphenyldihydropyrazine**, melting at 187°, becomes pyridazine, by heating it or by treating it with chromic acid. 1,3,4,6-**Tetraphenyldihydropyridazine**, $C_4H_2(C_6H_5)_4N_2$, melting at 149°, is obtained from desylacetophenone and phenylhydrazine. It yields 1,3,4-triphenylpyrazole (p. 483) (A. **289**, 310) upon dry distillation:

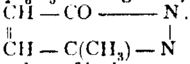


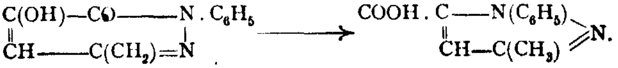
See below for the *ketodihydropyridazines* or *pyridazones*.

The ring-homologues of the pyrazolones are *ketotetrahydropyridazines* or *pyridazinones* (B. **28**, R. 68), and as these are formed from the hydrazones of β-ketonic esters, so the pyridazinones are prepared from γ-ketonic ester hydrazones (p. 126):

Phenylhydrazone of Lævulinic Ester — 1-Phenyl-3-methyl Pyridazinone.

The pyridazinones are not so stable as the pyrazolones.

Pyridazinone, $C_4H_6ON_2$, is an oil, boiling at 170°. It results from saponification and by the removal of CO_2 from **pyridazinone 3-carboxylic ester**, $C_4H_5ON_2 . CO_2R$, melting at 172°. This is a condensation-product of hydrazine with succinylo-formic ester, or formyl succinic ester (B. **28**, R. 239). Pyridazinone is readily decomposed by boiling alkalies, with the splitting-off of hydrazine. 3-**Methyl Pyridazinone**, melting at 94°, and 3-**Phenyl Pyridazinone**, melting at 149°, are prepared from lævulinic ester and benzoyl propionic ester. 3-**Phenylpyridazinone 5-carboxylic ester**, melting at 156°, is obtained from benzoyl propionic ester and hydrazine hydrate (B. **28**, R. 68). **1-Phenyl-3-methyl Pyridazinone**, $C_4H_4(CH_3)ON_2C_6H_5$, melting at 107° and boiling at 340–350°, yields **1-Phenyl-3 methyl pyridazone**, , on treatment with PCl_5 and ice-water. It contains two atoms less of hydrogen. It melts at 82°. *Phenylmethylchlorpyridazone* is formed at the same time, and can be converted by $NaOC_2H_5$ into *ethoxyphenylmethylpyridazone*. This on saponification becomes *oxyphenylmethylpyridazone*, which sustains rearrangement into 1-phenyl-3-methylpyrazole-5-carboxylic acid on being heated to 170° with hydrochloric acid (p. 485):



Maleïc Acid Hydrazine, $\begin{array}{l} CH-CO-NH \\ \| \qquad\quad\;\; | \\ CH-CO-NH \end{array}$, melting above 250°, is *diketotetrahydropyridazine*, which is formed, together with isomeric maleïc hydrazil, or n-amidomaleïnimide, from maleïc anhydride and hydrazine (B. **28**, R. 429). *Diketohexahydropyridazines*, or *ortho-piperazones*, are cyclic hydrazides of the succinic acid series, which are produced on heating the chlorides of these acids with the hydrazine hydrochlorides (p. 129): **n-Phenylortho-piperazone,** $\begin{array}{l} CH_2-CO-N.C_6H_5 \\ | \qquad\qquad\quad | \\ CH_2-CO-NH \end{array}$ (1, 449).

II. **Benzorthodiazines.**—There are two isomeric benzorthodiazines, depending upon whether the benzene ring attaches itself to the C-atom (3) and (4) or (4) and (5) of orthodiazine. The **cinnolines and phthalazines** correspond to these two isomerides:

Cinnoline Phthalazine.

Cinnoline, $C_6H_4\Big\langle\begin{array}{l} CH=CH \\ N=\!=\!=N \end{array}$, melting at 39°, is a strong base. It is poisonous. Its *iodmethylate* melts at 168°.

All the cinnoline derivatives known at present have been obtained from **oxycinnoline carboxylic acid,** $C_6H_4[C_2N_2(OH)(COOH)]$, melting at 260°, which is produced on digesting o-phenylpropiolic acid diazochloride with water (p. 284):

$$C_6H_4\Big\langle\begin{array}{l} C\equiv C.COOH \\ N_2(OH) \end{array} \longrightarrow C_6H_4\Big\langle\begin{array}{l} C(OH)-C.COOH \\ N=\!=\!=N \end{array}.$$

The acid loses CO_2 and becomes **oxycinnoline,** $C_8H_5N_2(OH)$, melting at 225°. PCl_5 converts this into **chlorcinnoline,** $C_8H_5N_2Cl$, the chlorine atom of which may be easily replaced by OH, OC_2H_5, NHC_6H_5, etc. Iron filings and sulphuric acid reduce chlorcinnoline to **dihydrocinnoline,** $C_6H_4(C_2H_4N_2)$, melting at 88°, which mercuric oxide oxidizes to cinnoline (B. **25**, 2847; **30**, 521).

Phthalazine, $C_6H_4\Big\langle\begin{array}{l} CH=N \\ CH=N \end{array}$, melting at 91°, and boiling at 316° (its chlorhydrate melts at 231°), is produced when a hydrazine solution acts upon ω-tetrachlor-, or, better, tetrabrom-o-xylene (p. 233): $C_6H_4\Big\langle\begin{array}{l} CHBr_2 \\ CHBr_2 \end{array} + \begin{array}{l} H_2N \\ H_2N \end{array} \longrightarrow C_6H_4\Big\langle\begin{array}{l} CH=N \\ CH=N \end{array}$. Phthalazine and methyl iodide form an *iodmethylate*, $C_8H_6N_2.ICH_3$, melting at 235–240°, which silver oxide converts into n-methylphthalazone, and caustic potash into n-methylphthalazone and **dihydro-n-methylphthalazine,** $C_6H_4\Big\langle\begin{array}{l} CH=N \\ CH_2-NCH_3 \end{array}$, which oxidizes very rapidly in the air to n-methylphthalazone (see the allied rearrangements of the alkyl quinolinium iodides (p. 544). Sodium amalgam reduces phthalazine to **tetrahydrophthalazine,** $C_6H_4\Big\langle\begin{array}{l} CH_2.NH \\ CH_2.NH \end{array}$, while with zinc-dust and hydrochloric acid the product is o-xylylene diamine, $C_6H_4(CH_2NH_2)_2$ (B. **26**, 2210; **28**, 1830, 2210). **Chlorphthalazine,** $C_6H_4(C_2HClN_2)$, melting at 113°, as well as **methyl-, propyl-, and isobutyl chlorphthalazone,** melting at 130° and 67° (the third being an oil), result from the action of $POCl_3$ upon phthalazone and alkylic phthalazones. The reduction of these chlorides

leads to derivatives of isoïndol (p. 232). Thus, chlorphthalazine forms *dihydroisoïndol*, $C_6H_4{<}{CH_2 \atop CH_2}{>}NH$ (p. 462); and methyl chlorphthalazine, *methyl isoïndol*, $C_6H_4{<}{C(CH_3) \atop CH_2}{>}N$, which yields dihydromethylisoïndol upon further reduction. The homologues behave similarly (B. 29, 1434).

Ketodihydrophthalazines, phthalazones, have been obtained from aromatic o-aldehydo- and ketone carboxylic acids by means of the hydrazines:

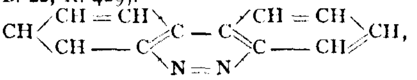
$$C_6H_4{<}{CHO \atop COOH} + {H_2N \atop H_2N} \longrightarrow C_6H_4{<}{CH = N \atop CO = NH}$$

Phthalaldehydic Acid — Phthalazone.

Phthalazone, $C_8H_6ON_2$, melting at 183° and boiling at 337°, combines with alcoholic potash to *potassium-phthalazone,* $C_8H_5ON_2K$. Acetyl chloride converts it into n-*acetyl-phthalazone,* while methyl iodide converts it into phthalazine iodmethylate.

c-Methyl Phthalazone, $C_6H_4{<}{C(CH_3) = N \atop CO —— NH}$, melting at 220° and boiling at 348°, is obtained from o-acetophenone carboxylic acid (B. 26, 524, 535). c-**Propyl-, Isobutyl-,** and **Benzyl Phthalazone** melt at 156°, 113°, and 152° (B. 29, 1434).

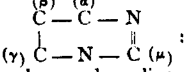
The cyclic hydrazides of the o-phthalic acids are *diketophthalazines.* They correspond to the orthopiperazones (p. 585), and can therefore be designated benzorthopiperazones: **Phthalyl Hydrazine,** $C_6H_4{<}{CO — NH \atop CO — NH}$, melting beyond 250°, results from the action of hydrazine upon phthalic ester, chloride, or anhydride (J. pr. Ch. [2], 52, 447; 54, 66). **Phthalyl Phenylhydrazine** (p. 240) results when phthalyl phenylhydrazide is heated (B. 28, R. 429).

III. **Phenazone,**  is a *dibenzo-ortho-diazine.* It consists of yellow needles, melting at 156°. When o_2-dinitrodiphenyl is reduced with sodium amalgam and methyl alcohol, an intramolecular formation of the azo-group occurs:

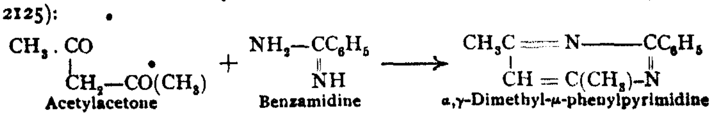
$$C_6H_4{<}NO_2 \quad O_2N{>}C_6H_4 \longrightarrow C_6H_4{<}N = N{>}C_6H_4.$$

Phenazone dioxide and *phenazone monoxide* are intermediate products. Phenazone is also formed on heating diphenylene-o_2-dihydrazine with hydrochloric acid to 150°. **Dihydrophenazone,** $C_{12}H_8(N_2H_2)$ (B. 24, 3083), is formed in the reduction of phenazone with tin and hydrochloric acid.

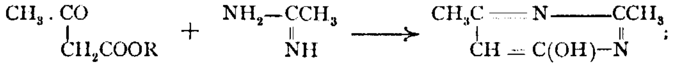
Phenazone is isomeric with phenazine (p. 598). It may also be regarded as derived from phenanthrene by replacing the intermediate CH-groups by N-atoms. Phenanthridine will then form the intermediate step. The relations of phenazone to orthodiazine, or pyridazine become evident from its oxidation to pyridazine tetracarboxylic acid by potassium permanganate (p. 584). **Tolazone,** $(C_7H_6)_2N_2$, melting at 187°, is prepared from a_2-dinitroditolyl (B. 26, 2239).

B. **Metadiazines,**  : I. Metadiazines, or **Pyrimidines,** are the analogues of the imidazoles or glyoxalines (p. 496), and, like these, can be viewed as cyclic amidines. Pyrimidines are produced:

1. From amidines of fatty or aromatic carboxylic acids and β-diketones (Pinner, B. 26, 2125):

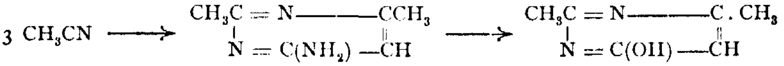


Similarly, amidines and trimethylene bromide yield tetrahydropyrimidines, while oxypyrimidines result if β-ketonic esters be employed (B. **23**, 3820):



and with β-ketone dicarboxylic esters, oxypyrimidine carboxylic esters are produced (compare action of acetmalonic ester upon amidines, B. **23**, 161).

2. A rather remarkable formation of the pyrimidines is that due to the polymerization of nitriles (cyan-alkyls) when they are heated to 150° with sodium or sodium alcoholate (1, 267). The *cyan-alkines*, resulting in this way, are amidopyrimidines, because they change to oxypyrimidines on treatment with nitrous acid, and these are identical with the oxypyrimidines prepared by method of formation (1) (B. **22**, R. 327):



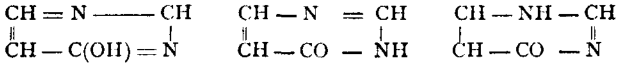
The course of the reaction is not yet fully explained. Probably dicyanalkyls are the first products (1, 267).

Cyanalkines are also obtained when sodium or sodium alcoholate acts upon mixtures of two alkyl cyanides.

μ,α,γ-**Phenyl Dimethyl Pyrimidine**, $C_4H(CH_3)_2(C_6H_5)N_2$ (see above), melts at 83° and boils at 276° (B. **25**, 2125). α,μ-**Diethyl-β-methyl Pyrimidine**, *Cyanconine*, $C_4H(C_2H_5)_2(CH_3)N_2$, boiling at 205°, has a narcotic odor and acts similarly to conine (see this). It is prepared from cyanethine by successive conversion into the corresponding oxypyrimidine, chlorpyrimidine, and reduction of the latter (B. **22**, R. 328). Consult B. **28**, 476, R. 67, for additional alkyl pyrimidines.

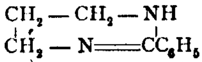
μ,α-**Dimethyl-γ-amidopyrimidine, Cyanmethine**, $C_4H(CH_3)_2(NH_2)N_2$, melting at 180°, and μ,α-**diethyl-β-methyl-γ-amidopyrimidine, Cyanethine**, $C_4(C_2H_5)_2(CH_3)(NH_2)N_2$, melting at 189°, are obtained from methyl and ethyl cyanide, and, like the rest of the cyanalkines, are strongly alkaline bases. **Cyanbenzyline**, $C_4H(CH_2C_6H_5)_2(C_6H_5)(NH_2)N_2$, melts at 106° (B. **29**, R. 787).

The *oxypyrimidines* possess both a phenol and a basic character. PCl_5 converts them into *chlorpyrimidines*. Derivatives of the keto- or pyrimidone form are obtained from the oxypyrimidines. They correspond to the three possible formulas:



μ-**Phenyl Oxypyrimidine**, μ-*Phenyl Pyrimidone*, $C_4H_3ON_2(C_6H_5)$, melting at 208° and boiling at 260–263° (30 mm.), results upon heating its *carboxylic acid*. μ-**Phenyl Pyrimidone-carboxylic acid**, $C_4H_2ON(C_6H_5)(CO_2R)$, the ester of the preceding acid, melts at 214° and is produced by condensing dicarboxyglutaconic ester with benzamidine or benzamidoxime. Its silver salt and ethyl iodide form γ-**ethoxy-μ-phenyl-β-carboxylic ester**, melting at 59° (B. **30**, 1488, 1564).

μ,α-**Dimethyl-γ-oxypyrimidine**, melting at 192°, results from acetoacetic ester and acetamidine, or when nitrous acid acts upon cyanmethine.

Hydropyrimidines: μ-**Phenyl Tetrahydropyrimidine**, , is formed from benzamidine and trimethylene bromide (B. **26**, 2122).

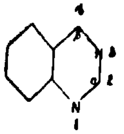
Ketotetrahydropyrimidines are obtained from the condensation of diamido-acetone and acid chlorides (B. **25**, 1564; B. **27**, 277):

$$\begin{array}{l} CO-CH_2-NH_2 \\ | \\ CH_2-NH_2 \end{array} + C_6H_5COCl \longrightarrow \begin{array}{l} CO-CH_2-NH \\ | \qquad\qquad\quad | \\ CH_2-N\text{——}C.C_6H_5 \end{array}$$

Diamido-acetone — μ-Phenyl-β-ketotetrahydropyrimidine, m. p. 91°.

The **uracil derivatives**, which are closely allied to uric acid, are also keto-derivatives of pyrimidine hydrides. *Uric acid* must be considered as the ureïde of isodialuric acid, a *diketodioxytetrahydropyrimidine*. It represents the naphthalene-like union of the pyrimidine ring with the imidazole ring, $\begin{array}{l} CO-NH-C-NH \\ \| \qquad\qquad \| \qquad\quad >CO \\ NH-CO-C-NH \end{array}$ (see the *alloxazines*, B. **28**, 1968, and B. **28**, R. 909). The cyclic *ureïdes* and *guanides* of the malonic acid series (I, 507; B. **26**, 255), the ureïde of mesoxalic acid or *alloxan*, a *triketohexahydropyrimidine* (I, 508), etc., belong here.

II. **Benzometadiazines**: The benzometadiazines or benzopyrimidines are the *quinazolines*, sometimes called *phenmiazines*. They are metameric, on the one hand, with the phthalazines and the cinnolines, and, upon the other, with the quinoxalines (p. 594). They may also be viewed as derivatives of the quinolines or isoquinolines by the substitution of an azo-ring:



The simplest quinazoline is not known. Derivatives of it are produced when the acidyl compounds of o-amidobenzaldehyde or of o-amidobenzoketones (pp. 181, 190) are treated with alcoholic ammonia (B. **28**, 279):

$$C_6H_4<\begin{array}{l}CHO \\ NH.COCH_3\end{array} + NH_3 \longrightarrow C_6H_4<\begin{array}{l}CH=N \\ N\text{——}C.CH_3\end{array}$$

o-Acetamidobenzaldehyde — α-Methyl Quinazoline.

The quinazolines are stable tertiary bases which distil without decomposition. They take up alkyl iodides. Sodium and alcohol reduce them to dihydroquinazolines (B. **26**, 1385). Chromic acid in glacial acetic acid oxidizes the quinazolines, in which the CH-group adjacent to the benzene nucleus is free, to ketodihydroquinazolines (or oxyquinazolines, etc.).

α-Methyl Quinazoline, $C_8H_5(CH_3)N_2$, melts at 35° and boils at 238°. **α,β-Dimethyl Quinazoline** is an oil boiling at 249°. It is formed when ammonia acts upon o-acetamidophenone. **α-Phenylquinazoline**, $C_8H_5(C_6H_5)N_2$, melting at 101° and boiling above 300°, results when ammonia acts upon o-benzoylamidobenzaldehyde, as well as from o-amidobenzyl-benzamide instead of the expected dihydro-derivative. **α-Methyl-β-phenyl Quinazoline**, $C_8H_4(CH_3)(C_6H_5)N_2$, melts at 48°. It is obtained from o-acetamido-benzophenone. Chromic acid oxidizes it to **β-phenylquinazoline-α-carboxylic acid.**

Ketohydroquinazolines and PCl_5 yield chlorquinazolines. α- and **β-Chlorquinazo-**

lines, melting at 108° and 96°, are obtained from *α*- **and** *β*-quinazolons. *α*-**Chlor-***β*-**phenyl Quinazoline, melting at 113°, is made from** phenyl-*α*-quinazolon (B. **29**, 1310). *α,β*-**Dichlorquinazoline, melting at 115°,** is obtained from benzoylene urea (p. 592).

Dihydroquinazolines, containing the same atomic grouping, $\begin{matrix}-N\!=\!\!\searrow \\ -NH\!\nearrow\end{matrix}CR$, as the anhydro-bases of the o-phenylenediamines, the benzimidazoles (p. 499), are to be regarded as the ring homologues of the latter: as *anhydro-bases* of the o-*amidobenzylamines.* They result by the elimination of water from the acidyl compounds of o-amidobenzylamine and its substitution products (B. **24**, 3096; **25**, 3037; **27**, R. 74; **29**, R. 1131):

$$C_6H_4\begin{matrix}\diagup CH_2\!-\!NH \\ \diagdown NH_2 \quad COR\end{matrix} \xrightarrow{-H_2O} C_6H_4\begin{matrix}\diagup CH_2\!-\!NH \\ \diagdown N \!=\!=\! CR\end{matrix}$$

The reaction proceeds the same if the acidyl-group replaces the aromatic NH_2-residue. Further, the o-amidobenzylacidylamines can rearrange themselves to o-acidylamidobenzylamines (B. **26**, 1891, R. 374). The same anhydro bases may also be obtained by reducing the corresponding o-nitrobenzylamine compounds.

The dihydroquinazolines are rather strong bases, forming stable salts. Free imide-hydrogen in them is readily replaced by alkyls. Like the quinazolines, they yield keto-dihydroquinazolines upon oxidation. They decompose upon distillation with zinc-dust. Sodium and alcohol reduce them to tetrahydroquinazolines. It may be noted that three isomeric, hydrogenized dihydro-compounds are possible from each c-alkyl quinazoline:

$$\text{I. } C_6H_4\begin{matrix}\diagup CH_2\!-\!NH \\ \diagdown N \!=\!=\! CR\end{matrix}, \quad \text{II. } C_6H_4\begin{matrix}\diagup CH_2\!-\!N \\ \diagdown NH\!-\!CR\end{matrix}, \quad \text{III. } C_6H_4\begin{matrix}\diagup CH \!=\! N \\ \diagdown NH\!-\!CHR\end{matrix},$$

which, probably, adopting the nomenclature of the hydrobenzenes, might be distinguished by the prefixes Δ_1, Δ_2, and Δ_3. Only two isomerides are possible for the dihydroquinazoline itself:

Δ_1-**Dihydroquinazoline,** $C_6H_4\begin{matrix}\diagup CH_2\!-\!NH \\ \diagdown N \!=\!=\! CH\end{matrix}$, melting at 127°, results from the reduction of o-nitrobenzyl formamide (B. **24**, 3097), as well as by that of *α*-chlorquinazoline (see above).

n,(3)-**Phenyl Dihydroquinazoline,** $C_8H_7(C_6H_5)N_2$, melting at 95°, is prepared from o-nitrobenzylformanilide. Under the name of *orexine* it has been recommended as a stomachic.

α-**Methyl Dihydroquinazoline,** $C_8H_7(CH_3)N_2$, is obtained from o-amidobenzylacetamide. *β*-**Phenyl Dihydroquinazoline,** melting at 166°, is produced by reducing *α*-chlor-*β*-phenylquinazoline (B. **29**, 1310).

β-Ketodihydroquinazolines, β-quinazolons, are formed, just like the dihydroquinazolines, from the acidyl derivatives of o-amidobenzamide:

$$C_6H_4\begin{matrix}\diagup CO\!-\!NH_2 \\ \diagdown NH\,.\,COCH_3\end{matrix} \text{ or } C_6H_4\begin{matrix}\diagup CO\!-\!NH \\ \diagdown NH_2 \quad COCH_3\end{matrix} \longrightarrow C_6H_4\begin{matrix}\diagup CO\!-\!NH \\ \diagdown N \!=\!=\! C\,.\,CH_3\end{matrix}$$

Analogous products are obtained on heating acidyl derivatives of anthranilic ester with ammonia or with primary amines, or from anthranilic acid and the amides of fatty acids (B. 27, R. 516; 28, R. 783) (p. 213). *β*-**Ketodihydroquinazolines, as mentioned, are produced, in addition to these synthetic methods, by oxidizing quinazolines and dihydroquinazolines.**

a-Ketodihydroquinazolines, a-quinazolons, are produced when o-amidobenzaldehydes and -benzene ketones are heated with urea (B. **29**, 1300):

$$C_6H_4<\begin{matrix}CHO\\NH_2\end{matrix} + \begin{matrix}NH_2\\|\\CO—NH_2\end{matrix} \longrightarrow C_6H_4<\begin{matrix}CH = N\\ \quad\ \ |\\NH — CO\end{matrix}.$$

The quinazolons possess both feeble phenol and basic characters, hence can also be regarded as oxyquinazolines. They combine with alkyl iodides to n-alkyl derivatives of the keto-form. The isomeric *alkoxylquinazolines* are obtained from the *chlorquinazolines* (p. 589).

β-**Ketodihydroquinazoline,** *β-Oxyquinazoline*, $C_8H_6ON_2$, melting at 214°, is produced from anthranilic acid and formamide (J. pr. Ch. [2], **43**, 215; **51**, 564). Methyl iodide converts it into n-**methylketodihydroquinazoline,** $C_8H_5ON_2 . CH_3$, melting at 74°.

α-**Methyl-*β*-ketodihydroquinazoline,** melting at 232°, is obtained from o-acetamidobenzamide or o-amidobenzoylacetamide (see above), and also in the oxidation of *α*-methylquinazoline (B. **28**, 279). *α*-**Phenyl-*β*-ketodihydroquinazoline,** $C_8H_5(C_6H_5)NO_2$, melting at 236°, is made from phenylquinazoline or o-benzoylamidobenzamide. n-**Phenyl-*β*-ketodihydroquinazoline,** melting at 139°, is obtained by oxidizing n-phenyldihydroquinazoline (B. **24**, 3055).

α-**Ketodihydroquinazoline,** *α-Quinazolon*, is formed from o-amidobenzaldehyde and urea, as well as by oxidizing benzylene-*ψ*-thiurea (p. 177) with $Ba(MnO_4)_2$. *β*-**Phenyl-*α*-ketodihydroquinazoline,** melting at 251°, is prepared from o-amidobenzophenone and urea (B. **29**, 1310).

Tetrahydroquinazolines are produced by the reduction of quinazolines, dihydroquinazolines, and thiotetrahydroquinazolines. They also result in the condensation of o-amidobenzylamines with aldehydes (J. pr. Ch. [2], **53**, 414; **55**, 356). They may be readily decomposed into benzene ortho-derivatives:

Tetrahydroquinazoline, $C_6H_4<\begin{matrix}CH_2 — NH\\ \quad\ \ |\\NH — CH_2\end{matrix}$, is amorphous, and results from the interaction of o-amidobenzylamine and formaldehyde. n(3)-**Phenyl Tetrahydroquinazoline,** $C_6H_4(C_2H_5N . C_6H_5)$, melting at 119°, is derived from o-amidobenzylaniline and formaldehyde, also from phenyldihydro- and phenylthio-tetrahydro-quinazoline (B. **25**, 2858). *α*-**Phenyl Tetrahydroquinazoline** melts at 100° (B. **25**, 3033). See B. **29**, 1308, for *β*-**Phenyltetrahydroquinazoline.** n-**Dibenzoyl-*α*,*β*-dimethyl Tetrahydroquinazoline,** $C_8H_6(CH_3)_2N_2(COC_6H_5)_2$, melts at 155° (B. **26**, 1385).

a-Keto- and *thiotetrahydroquinazolines* correspond to the cyclic phenylene ureas and -thioureas (p. 502). They are, like these, produced when $COCl_2$ or CS_2 acts upon o-amidobenzylamines, or by the exit of NH_3 or amine from the urea derivatives of the o-amidobenzylamines (B. **25**, 2856; **27**, R. 74, etc.):

$$C_6H_4<\begin{matrix}CH_2 —NHC_6H_5\\NH—CO . NHC_6H_5\end{matrix} \text{ or } C_6H_4<\begin{matrix}CH_2—NC_6H_5\\ \quad\ \ |\\NH_2 \quad CONHC_6H_5\end{matrix} \longrightarrow C_6H_4<\begin{matrix}CH_2—N.C_6H_5\\ \quad\ \ |\\NH — CO\end{matrix} (+ NH_2C_6H_5)$$

$$C_6H_4<\begin{matrix}CH_2—NHC_6H_5\\NH_2\end{matrix} + CS_2 \longrightarrow C_6H_4<\begin{matrix}CH_2—NC_6H_5\\ \quad\ \ |\\NH —CS\end{matrix}.$$

Diketotetrahydroquinazolines are similarly produced from the o-amidobenzamides by means of $COCl_2$, $ClCO_2R$, etc., or from urea derivatives of o-amidobenzamide or of the anthranilic acids:

$$C_6H_4<\begin{matrix}CONH_2\\NH_2\end{matrix} + COCl_2 \longrightarrow C_6H_4<\begin{matrix}CO—NH\\ \quad\ \ |\\NH—CO\end{matrix}.$$

Keto- and tetrahydroquinazolines are indifferent bodies. Mention has already been made of their formation from benzometoxazine derivatives, the imido- and thiocoumazones, by heating them with aromatic amines. Oxidants convert them into diketotetrahydroquinazolines, which also result from the oxidation of imido coumazones (B. **27**, 2420). The diketotetrahydroquinazolines possess acid properties and dissolve only in alkalies. PCl_5 converts them into *dichlorquinazolines*.

n(3)-**Phenyl-α-ketotetrahydroquinazoline,** $C_8H_7 . ON_2 . C_6H_5$, melts at 189° (B. **27**, 74). **β-Phenyl-α-ketotetrahydroquinazoline,** melting at 193°, is obtained from o-amidobenzhydrol and urea, as well as from the corresponding phenylthiotetrahydroquinazoline. The latter is brominated, and the brom-dihydro phenylquinazoline is then converted by soda into ketoquinazoline (B. **29**, 1307).

α-Thiotetrahydroquinazoline, $C_8H_8SN_2$, melts at 211°. **n-Phenyl-α-thiotetrahydroquinazoline,** $C_8H_7SN_2 . C_6H_5$, melts at 260° (B. **27**, 2432). **β-Phenyl-α-thiotetrahydroquinazoline,** melting at 230°, is obtained from o-amidobenzhydrol and hydrosulphocyanic acid (B. **29**, 1305).

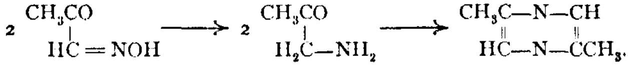
Diketotetrahydroquinazoline, Benzoylene Urea, $C_6H_4(C_2O_2N_2H_2)$, melts above 360° and sublimes. **n-Phenyl Diketotetrahydroquinazoline,** $C_6H_4(C_2O_2NHC_6H_5)$, melts at 272° (B. **27**, 974, 2410, R. 392; compare also B. **30**, 1682).

α-Thio-β-ketotetrahydroquinazoline, $C_6H_4(C_2OSN_2H_2)$, melting at 284°, is prepared from anthranilic ester and hydrosulphocyanic acid (B. **30**, 1098; C. 1897, I, 592).

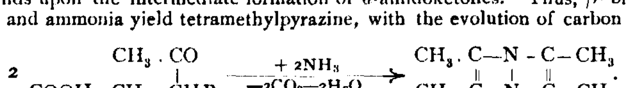
C. **Paradiazine,** $\begin{matrix}(\gamma)C - N - C(\beta) \\ | \qquad\quad | \\ (\delta)C - N - C(\alpha)\end{matrix}$: I. Paradiazines are the **pyrazines,** or *piazines,* which can be regarded as pyridines, the methine group of which is substituted in the γ-position by N. It is almost universally accepted that there is a "para-union" of the two N-atoms in the pyrazines, harmonizing with the formula $N\begin{matrix}\diagup CH = CH \diagdown \\ \diagdown CH = CH \diagup\end{matrix}N$ (Wolff, B. **26**, 722).

Pyrazines are formed (1) by condensing two molecules of α-amidoaldehydes and α-amidoketones, when an exit of water occurs. Hence they are called *aldines* or *ketines.*

Instead of isolating the amido-ketones, the solution of them obtained in the reduction of isonitrosoketones can be distilled with the addition of $HgCl_2$, the oxidizing agent (B. **26**, 1832, 2207):



(2) The synthesis of pyrazines from α-chlor- or bromketo-compounds and ammonia also depends upon the intermediate formation of α-amidoketones. Thus, β-bromlævulinic acid and ammonia yield tetramethylpyrazine, with the evolution of carbon dioxide:



Pyrazines occur also in the fermentation products of sugar. Thus, α,γ-dimethyl- and trimethyl-pyrazine have been isolated from fusel oil. Pyrazines also result in the action of ammonia upon grape-sugar. In this instance the products are pyrazine, methyl- and dimethyl pyrazines (B. **30**, 224; J. pr. Ch. [2], **54**, 481).

The pyrazines are feeble bases, which give a neutral reaction to litmus. They form readily dissociated salts with acids. Like the pyridines, they form characteristic compounds with metallic salts—*e.g.*, mercuric chloride, auric chloride, etc.

Sodium reduces the pyrazines to piperazines or hexahydropyrazines corresponding to the piperidines. Potassium permanganate oxidizes alkylic pyrazines to pyrazine carboxylic acids, which part with carbon dioxide very readily.

Pyrazine, $\begin{array}{c}CH - N - CH \\ \| \quad\;\; | \quad\;\; \| \\ CH - N - CH\end{array}$, melting at 55° and boiling at 115° (B. **27**, R. 396), is a substance smelling like heliotrope and subliming at the ordinary temperature. It is produced when amidoacetaldehyde or amidoacetal (1, 317) is distilled with a sublimate solution, also by eliminating carbon dioxide from the pyrazine carboxylic acids, and upon distilling piperazine with zinc-dust (B. **26**, R. 441).

Methyl Pyrazine, $C_4H_3(CH_3)N_2$, boiling at 135°, is obtained from its carboxylic acid (B. **28**, R. 551), and constitutes the chief constituent of the bases produced in the action of ammonia upon grape-sugar. α,γ-**Dimethyl Pyrazine**, *Ketine*, $C_4H_2(CH_3)_2N_2$, is an oil, boiling at 153°. It is formed in the reduction of isonitrosoacetone, and, together with pyridine bases and other alkylic pyrazines,—*e. g.*, α,γ,δ-**methyl diethyl pyrazine**, b. p. 179° (B. **24**, 4105; **26**, R. 442),—upon distilling glycerol with ammonium salts.

α,δ-**Dimethyl Pyrazine** melts at 48° and boils at 155° (J. pr. Ch. [2], **54**, 492). **Trimethyl Pyrazine**, boiling at 172°, is produced on heating the brom-methylate of α,γ-dimethyl pyrazine (B. **29**, R. 980). **Tetramethyl Pyrazine**, $C_4(CH_3)_4N_2(+3H_2O)$, melts at 86° (75°) and boils at 190°. It is produced when ammonia acts upon β-bromlævulinic acid (1, 381), or by reducing β-isonitroso-lævulinic acid (B. **25**, 1723).

α,γ-**Diphenyl Pyrazine**, $C_4(C_6H_5)_2H_2N_2$, melting at 196°, results from α-amido-acetophenone, and from n-dibenzyldihydro-α,γ-diphenylpyrazine, $C_7H_7N{<}{\begin{array}{l}C(C_6H_5) = CH \\ CH = C(C_6H_5)\end{array}}{>}NC_7H_7$, by the exit of toluene (B. **27**, R. 135). The isomeric α,δ-**diphenyl pyrazine**, melting at 89°, is similarly formed from n-benzyl-dihydro-α,δ-diphenyl pyrazine (see below) by the splitting-off of toluene. α,γ-**Diphenyl-dimethyl Pyrazine**, $C_4(C_6H_5)_2(CH_3)_2N_2$, melting at 126°, is prepared from isonitroso-phenylacetone (B. **29**, R. 548).

Tetraphenyl Pyrazine, *Tetraphenylaldine*, $C_4(C_6H_5)_4N_2$, melting at 246°, is made by reducing the benzil monoximes or dioximes (p. 373) (B. **27**, 213).

Pyrazine Monocarboxylic Acid, melting with decomposition at 230°, **pyrazine dicarboxylic acid**, $C_4H_2(COOH)_2N_2(+2H_2O)$, melting at 256°, and **pyrazine tetracarboxylic acid**, $C_4(COOH)_4N_2$, melting at 205°, etc., result upon oxidizing the methylated pyrazines with potassium permanganate. Consult B. **26**, R. 442, for other pyrazine carboxylic acids.

Dihydropyrazines, containing two imide groups, are prepared, together with the isomeric indols, in the action of anilines upon α-alkylamidoketone derivatives, $RHNC-H_2 . CO-$, or from α-bromketones and primary amines.

n-Dibenzene Sulphon-dihydropyrazine, $C_6H_5SO_2N{<}{\begin{array}{l}CH = CH \\ CH = CH\end{array}}{>}NSO_2C_6H_5$, melting at 163°, is obtained from benzene sulphamidoacetal (B. **26**, 98). **n-Diphenyl-dihydro-α,γ-diphenyl Pyrazine**, *diphenyldiisoïndol*, $C_4H_2(C_6H_5)_2(N . C_6H_5)_2$, melting at 181°, is formed from aniline and phenacyl bromide (p. 248). Different dihydropyrazine derivatives, like **n-dibenzyl-α,γ-diphenyldihydropyrazine**, melting at 163°, **n-benzyl-α,δ-diphenyldihydropyrazine**, etc., are produced by the condensation of benzylamine and phenacyl bromide (B. **27**, R. 134).

Dihydropyrazines, with tertiary N-atoms, are obtained from 1,2-diketones and ethylene diamine (B. **22**, 346; **26**, R. 1009):

$$\begin{array}{l}CH_2-NH_2 \\ | \\ CH_2-NH_2\end{array} + \begin{array}{l}CO . C_6H_5 \\ | \\ CO . C_6H_5\end{array} \longrightarrow \begin{array}{l}CH_2-N = C . C_6H_5 \\ | \qquad\quad\;\; | \\ CH_2-N = C . C_6H_5\end{array}$$

Benzil   **α,β-Diphenyl-γ,δ-dihydropyrazine.**

n-Diphenyl Tetrahydrophenylpyrazine, $\begin{array}{l} CH_2 - N(C_6H_5) - CH \\ | \qquad\qquad\qquad\quad \| \\ CH_2 - N(C_6H_5) - CC_6H_5 \end{array}$, is similarly formed from ethylene diphenyl diamine and phenacyl bromide (B. **26**, R. 93).

Hexahydropyrazines, piperazines, have already been discussed on p. 314 as cyclic dialkylene imides. In addition to the synthetic methods given there, the piperazines are also prepared by the reduction of the pyrazines with sodium and alcohol (B. **26**, 724):

μ-Methyl Piperazine, $C_4H_9(CH_3)N_2$, boils at 155°.

Di- and poly-alkylic piperazines occur each in two stereoisomeric forms: **Di-, Tri-, Tetramethyl Piperazine**—see J. pr. Ch. [2], **55**, 49. Consult B. **29**, R. 384, for

methenyl piperazine, $\begin{array}{c} \diagup CH_2 - CH_2 \diagdown \\ N \text{———} CH_2 \text{———} N \\ \diagdown CH_2 - CH_2 \diagup \end{array}$ (?), made from piperazine and formaldehyde.

n-Diphenyl Piperazine, $\begin{array}{l} CH_2 - N(C_6H_5) - CH_2 \\ | \qquad\qquad\qquad\quad | \\ CH_2 - N(C_6H_5) - CH_2 \end{array}$, melting at 163°, results from the interaction of ethylene bromide and aniline (B. **22**, 1777). **n-Dibenzyl Piperazine,** melting at 92°, is also produced when caustic potash acts upon bromethylbenzylamine.

The cyclic double-acid amides are *α,γ-diketopiperazines*. They have already received consideration (I, 358) after the α-amidocarboxylic acids. **Diphenyl Diketopiperazine,** *diphenyl diacipiperazine*, $\begin{array}{l} CH_2 - N(C_6H_5) - CO \\ | \qquad\qquad\qquad\quad | \\ CO \;- N(C_6H_5) - CH_2 \end{array}$, is formed from anilido-acetic acid—see p. 84. Consult B. **25**, 2919, 3275, etc., for stereoisomeric diacipiperazines.

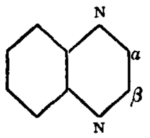
α,β-Diketopiperazines are produced in the condensation of oxalic acid with derivatives of ethylene diamine (B. **23**, 2028):

$$\begin{array}{l} CH_2-NHC_6H_5 \\ | \\ CH_2-NHC_6H_5 \end{array} + \begin{array}{l} COOH \\ | \\ COOH \end{array} \longrightarrow \begin{array}{l} CH_2-N(C_6H_5)-CO \\ | \qquad\qquad\qquad\; | \\ CH_2-N(C_6H_5)-CO \end{array}$$

n-Diphenyl-α,β-diketopiperazine.

Chromic acid oxidizes this diketopiperazine to a tetraketopiperazine.

II. Benzoparadiazines: Quinoxalines.—



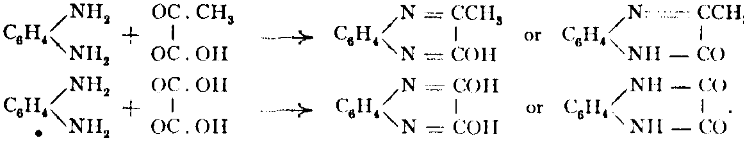
The quinoxalines, just like the benzimidazoles, are condensation products of o-diamines (p. 95). They result:

1. By the condensation of o-phenylenediamines with glyoxal and 1,2-diketone compounds (Hinsberg, A. **237**, 327):

$$C_6H_4\begin{array}{l} \diagup NH_2 \\ \diagdown NH_2 \end{array} + \begin{array}{l} COH \\ | \\ COH \end{array} \xrightarrow{-2H_2O} C_6H_4\begin{array}{l} \diagup N = CH \\ \qquad\quad | \\ \diagdown N = CH \end{array}.$$

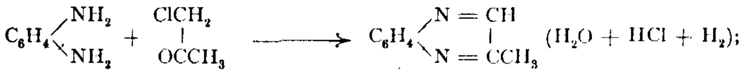
Similarly, benzil yields α,β-diphenylquinoxaline; dioxytartaric acid, α,β-quinoxaline carboxylic acid; etc. The reactions are very complete, even at the ordinary temperatures.

a-Ketone carboxylic acids—*e. g.*, pyroracemic acid and mesoxalic acid—become *oxyquinoxalines*, while oxalic acid yields *dioxyquinoxalines* (B. **30**, 768):

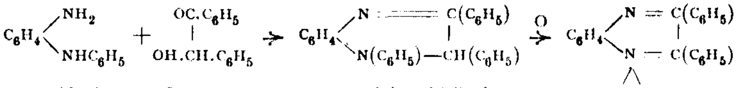


The o-naphthylenediamines react like the o-phenylenediamines, forming *naphthoquinoxalines*. The tetra-amidobenzenes yield *benzodiparadiazines*.

2. *a*-Chlorketo-compounds, *a*-aldehyde alcohols, and *a*-ketone alcohols—*e. g.*, benzoïn, furoïn, arabinose, and glucose—condense with o-phenylenediamines. Water and hydrogen are eliminated and quinoxalines remain:



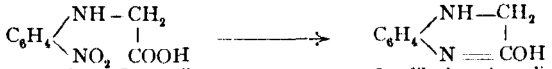
with monoalkylic o-phenylenediamines, on the other hand, the products are dihydroquinoxalines, which ferric chloride oxidizes to azonium bases of the quinoxalines (B. **24**, 719, 1875; **25**, 1627):



o-Amido-diphenylamine — Benzoïn — n-*a*,*β*-Triphenyl Dihydroquinoxaline — C_6H_5 OH Phenyl Stilbazonium Hydroxide.

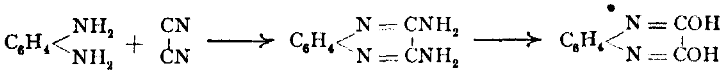
The azonium bases are immediately produced by the action of monoalkylic or phenylated o-diamines upon 1,2-diketones (B. **25**, 1010; **27**, 2355). See also B. **25**, 1627.

3. o-Nitrophenyl *a*-amido-fatty acids, when reduced, yield *oxydihydroquinoxalines*, which are also obtained from o-phenylenediamines and *a*-haloid fatty acids (A. **292**, 250):

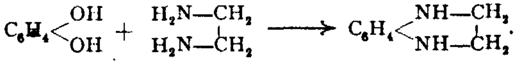


a-Nitrophenyl Glycocoll — *a*-Oxydihydroquinoxaline.

4. o-Phenylenediamines condense with cyanogen to *diamido-quinoxalines*, which dilute hydrochloric acid changes to dioxyquinoxalines:



5. *Tetrahydroquinoxalines* are produced in the condensation of dioxybenzenes with alkylenediamines:



Behavior: The quinoxalines are feeble monacid bases. Their odor resembles that of quinoline or piperidine. They are readily soluble in alcohol and ether, and more sparingly soluble in hot than in cold water. They are stable in the presence of oxidizing agents, while reducing agents convert them into hydroquinoxalines.

Quinoxaline, $C_8H_6N_2$, is obtained from o-phenylenediamine and glyoxal, by digesting the aqueous solution at 60° with sodium bisulphite. It melts at 27° and boils at 229°. Its **iodmethylate** melts with decomposition at 175°.

Toluquinoxaline, $C_6H_3(CH_3):N_2C_2H_2$, obtained in a similar way from toluylenediamine, boils at 245°. α,β **Dimethyl Toluquinoxaline,** $C_6H_3(CH_3):N_2C_2(CH_3)_2$, from diacetyl and toluylenediamine, melts at 54° and boils at 270°. α,β **Diphenyl Quinoxaline,** $C_6H_4N_2(C_6H_5)_2$, melts at 124° (B. **27**, 2181).

Bz-Chloroxy-α,β-diphenyl Quinoxaline has been recommended as an indicator in alkalimetry under the name of *luteol* (B. **28**, R. 628).

Oxyquinoxaline, $C_6H_4[N_2C_2H(OH)]$, melting at 265°, is made from its carboxylic acid (see below).

α-Methyl-β-oxytoluquinoxaline, $CH_3C_6H_3[N_2C_2(CH_3)(OH)]$, melting at 220°, and **α Phenyl-β-oxytoluquinoxaline,** $CH_3C_6H_3[N_2C_2(C_6H_5)(OH)]$, melting at 196°, are prepared from toluylenediamine with pyroracemic acid and phenylglyoxylic acid. They are soluble both in alkalies and in acids. The solutions of the first are colorless, and those of the second yellow in color. **α,β-Dioxyquinoxaline,** $C_6H_4[N_2C_2H_2O_2]$, from o-phenylenediamine and oxalic acid, or α,β-diamidoquinoxaline (see above) by means of hydrochloric acid is converted by PCl_5 into **α,β Dichlorquinoxaline,** melting at 150°. When the latter is digested with o-phenylenediamine a condensation results, the solutions of which are yellow in color and exhibit an intense yellow-green fluorescence. This fact has given it the name **fluoflavine,** $C_6H_4:(N_4C_2H_2):C_6H_4$, melting at 360°. It loses two hydrogen atoms when it is oxidized, and becomes **Quinoxalophenazine,** $C_6H_4:(N_4C_2):C_6H_4$ (B. **29**, 784):

$$C_6H_4\left\langle\begin{array}{l}N=CCl\\N=CCl\end{array}\right. + \left.\begin{array}{l}NH_2\\NH_2\end{array}\right\rangle C_6H_4 \rightarrow C_6H_4\left\langle\begin{array}{l}N=C—NH\\ \quad\;\; |\\N=C—NH\end{array}\right\rangle C_6H_4 \rightarrow C_6H_4\left\langle\begin{array}{c}N—C—N\\ | \quad \| \quad |\\N—C—N\end{array}\right\rangle C_6H_4.$$

α,β-Dioxynaphthoquinoxaline, *Naphthylene Oxamide*, $C_{10}H_6(N_2C_2O_2H_2)$ (B. **30**, 772).

α,β-Quinoxaline Dicarboxylic Acid, $C_6H_4[N_2C_2(COOH)_2](+2H_2O)$, from dioxytartaric acid and o-phenylenediamine, melts at 190° with decomposition (B. **27**, 2185). It forms an *anhydride*, $C_6H_4\left\langle\begin{array}{l}N=C—CO\\ \quad\;\; |\\N=C—CO\end{array}\right\rangle O$, melting at 251°. Ammonia converts the latter into quinoxaline dicarbonamic acid, which with bromine and caustic potash yields **α-amidoquinoxaline-β-carboxylic acid,** $C_6H_4[N_2C_2(NH_2)(COOH)]$, melting with decomposition at 210° (B. **28**, 1657).

α-Oxyquinoxaline-β-carboxylic Acid, $C_6H_4[N_2C_2(OH)(COOH)]$, melting at 265° with decomposition, is produced by saponifying the acid ureïde produced in the interaction of alloxan and o-phenylenediamine (A. **292**, 248).

Hydroquinoxalines: The dihydroquinoxalines are distinguished by their yellow-green fluorescence:

Dihydro-α,β-diphenyl Quinoxaline, $C_6H_4\left\langle\begin{array}{l}N=CC_6H_5\\ \quad\;\;\; |\\NH—CHC_6H_5\end{array}\right.$, melts at 146°, and is produced in the reduction of diphenylquinoxaline with stannous chloride, or from benzoïn and o-phenylenediamine (B. **24**, 1870; **27**, 2182). **n-Methyl Dihydro-α,β-diphenyl Quinoxaline** (B. **25**, 1632) is oxidized to *methylphenostilbazonium hydroxide*,

$$C_6H_4\left\langle\begin{array}{l}N=C.C_6H_5\\ \quad\;\; |\\N=C.C_6H_5\\ \;\wedge\\ CH_3\;OH\end{array}\right.,$$ (see p. 595).

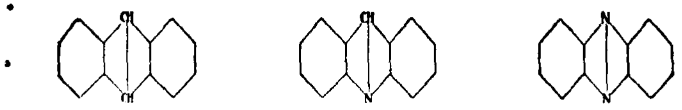
n-Methyl-ketodihydro-β-methyl Quinoxaline, n,β-*Dimethyl Quinoxalone*, $C_6H_4\left\langle\begin{array}{l}N=CCH_3\\ \qquad\quad |\\N(CH_3)—CO\end{array}\right.$, melts at 78° and boils at 308°. It results from the condensation of methyl-o-phenylenediamines and pyroracemic acid (B. **25**, 1630).

Tetrahydroquinoxaline, $C_8H_{10}N_2$, melting at 97° and boiling at 289°, is obtained from pyrocatechol and ethylenediamine (B. **21**, 378), or by saponifying its *dibenzosul-*

phonic derivative, $C_6H_4(NSO_2C_6H_5)_2>(CH_2)_2$—the reaction-product of ethylene bromide and dibenzene sulphon-o-phenylenediamine (B. **28**, R. 756).

α,β-**Diphenyl Tetrahydroquinoxaline**, $C_8H_8N_2(C_6H_5)_2$, is produced in two isomeric forms, melting at 105° and 142°, when diphenylquinoxaline is reduced with sodium and alcohol (B. **27**, 2184).

III. *Dibenzoparadiazines:* **Phenazine Group.**—Phenazine is analogous in constitution to anthracene and acridine:



Anthracene　　　Acridine　　　Phenazine.

On the other hand, it is, in its methods of formation and general deportment, very closely related to the dibenzo-derivatives of paroxazine and parathiazine (pp. 581, 583):

$$C_6H_4\begin{matrix}\diagup O \diagdown\\ \diagdown NH \diagup\end{matrix}C_6H_4 \qquad C_6H_4\begin{matrix}\diagup S \diagdown\\ \diagdown NH \diagup\end{matrix}C_6H_4 \qquad C_6H_4\begin{matrix}\diagup N \diagdown\\ | \\ \diagdown N \diagup\end{matrix}C_6H_4$$

Dibenzoparoxazine, Phenoxazine　　Dibenzoparathiazine, Thiodiphenylamine　　Dibenzoparadiazine, Phenazine.

It is the parent substance of an extensive class of dyestuffs, which are to some degree quite important from the technical standpoint—*e. g.*, the eurhodines, toluylene-red, the indulines, safranines, etc., which are in part derived from phenazine itself and partly from higher, condensed paradiazines—*e. g.*, naphthophenazine, naphthazine, etc.

Methods of Formation: 1. Phenazines result by the exit of water and hydrogen in the condensation of o-diamines and o-dioxybenzenes:

$$C_6H_4<\begin{matrix}NH_2\\NH_2\end{matrix} + \begin{matrix}OH\\OH\end{matrix}>C_6H_4 \longrightarrow C_6H_4<\begin{matrix}N\\|\\N\end{matrix}>C_6H_4.$$

2. Azines are also produced from o-diamines and o-quinones—*e. g.*, β-naphthoquinone, phenanthraquinone, croconic acid, etc.:

$$C_6H_4\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} + \underset{\beta\text{-Naphthoquinone}}{\begin{matrix}OC-CH=CH\\ | \qquad\quad |\\ OC-\!\!-\!\!-\!\!-C_6H_4\end{matrix}} \longrightarrow \underset{\text{Phenonaphthazine.}}{C_6H_4\begin{matrix}\diagup N-C-CH=CH\\ | \quad \| \qquad\quad |\\ \diagdown N-C-\!\!-\!\!-C_6H_4\end{matrix}}$$

Isatin and o-phenylenediamine similarly yield *indophenazine*, $\begin{matrix}C_6H_4\,.\,C-N\\ | \qquad \| \quad\; |\\ NH-C-N\end{matrix}>C_6H_4$ (B. **29**, 800). On the other hand, *azonium bases* result if monosubstituted o-diamines and o-quinones are condensed (see quinoxalines, p. 594):

$$C_{10}H_6\begin{matrix}\diagup NH_2\\ \diagdown NHC_6H_5\end{matrix} + \begin{matrix}CO-C_6H_4\\ | \qquad |\\ CO-C_6H_4\end{matrix} \longrightarrow C_{10}H_6\begin{matrix}\diagup N-C-C_6H_4\\ \quad \| \quad |\\ \diagdown N-C-C_6H_4\\ \wedge \\ C_6H_5\;\; OH\end{matrix}$$

o-Amidonaphthylphenylamine　　Phenanthraquinone　　Phenylnaphthophenanthrazonium Hydroxide.

Such *azonium* compounds are also produced by the action of azines and alkyl iodides, and by the deamidation of induline and safranine bases (p. 600).

3. Furthermore, azines result in the oxidation of a mixture of o-diamines and α-naphthol:

$$C_6H_4<^{NH_2}_{NH_2} + C_{10}H_7OH \longrightarrow C_6H_4<^{N}_{N}>C_{10}H_6.$$

4. By the decomposition of o-anilido-(toluido-, etc.)-azo-bodies. Thus, o-anilidonaphthylazobenzene-sulphonic acid, produced by the combination of naphthylphenylamine with diazobenzene-sulphonic acid, breaks down, on boiling with dilute acids, into naphthophenazine and sulphanilic acid:

$$C_{10}H_6<^{N:NC_6H_4.SO_3H}_{NH.C_6H_5} \longrightarrow C_{10}H_6<^{N}_{N}>C_6H_4 + H_2N.C_6H_4.SO_3H$$

α-Anilidonaphthylazobenzene-sulphonic Acid — Naphthophenazine — Sulphanilic Acid.

Behavior: The phenazines are mostly yellow-colored, feebly basic bodies that cannot be distilled without suffering decomposition. They dissolve in concentrated sulphuric acid with a red to blue color. They are again precipitated upon addition of water. They combine with alkyl iodides to azonium iodides (p. 600). They are reduced to colorless, dihydro-compounds,—*e. g.*, *dihydrophenazine*, $C_6H_4<^{NH}_{NH}>C_6H_4$,—which are readily re-oxidized to azines.

Phenazine, $C_{12}H_8N_2$, was first obtained from calcium azobenzoate by distillation, and was called *Azodiphenylene* (p. 587), with which it is isomeric. It may also be prepared from o-phenylenediamine and pyrocatechin, and by conducting aniline vapors through a tube heated to redness, by the deamidation of amidophenazines, and upon boiling formazyl carboxylic ester, $CO_2R.C<^{N.NHC_6H_5}_{N:NC_6H_5}$, with concentrated acids (B. 25, 3205); together with various other products in the oxidation of o-amidodiphenylamine, $C_6H_4<^{NH.C_6H_5}_{NH_2}$ (B. 26, 383). It melts at 171°.

Ammonium sulphide reduces phenazine to *dihydrophenazine*. Consult A. 292, 260, for its reduction in acid solutions.

Toluphenazine, $CH_3.C_6H_3:N_2:C_6H_4$, melting at 117°, is obtained from toluylenediamine and pyrocatechol; also from o-amidophenyltolylamine and lead oxide (B. 29, 1873).

α,β-**Naphthophenazine**, $C_{10}H_6:N_2:C_6H_4$, melting at 142°, is produced, in addition to the common methods (see above), from naphthylphenylnitrosamine, $C_{10}H_7\diagdown\overset{NO}{\underset{N}{|}}\diagup C_6H_5$, just as acridine (p. 559) is obtained from formyldiphenylamine. Sym. α,β-**naphthazine**, $C_{10}H_6:N_2:C_{10}H_6$, melting at 243°, is formed in like manner from β,β-dinaphthylnitrosamine (B. 26, 185). Unsym. α,β-**Naphthazine**, melting at 283°, was first made by heating nitronaphthalene with lime (*naphthase*, Laurent, 1840), and was consequently long regarded as azonaphthalene. It was also prepared from α,β-naphthylenediamine and β-naphthoquinone. It is most easily made by condensing nitroso-β-naphthylamine and α-naphthylamine (B. 29, 2086). **Phenanthrophenazine**, $C_{14}H_8:N_2:C_6H_4$, melts at 217° and is obtained from phenanthraquinone and o-phenylenediamine.

The entrance of salt-forming groups, like NH_2 and OH, converts the phenazines into dyestuffs. In addition to the normal formulas, *para-quinoïd* pseudo-forms come into consideration for these amido- and oxyphenazines (eurhodines and eurhodols) (A. 290, 260):

$$C_6H_4<{N \atop N}>C_6H_3NH_2 \quad \text{or} \quad C_6H_4<{N= \atop NH}>C_6H_3:NH$$

Eurhodine;

$$C_6H_4<{N \atop N}>C_6H_3.OH \quad \text{or} \quad C_6H_4<{N= \atop NH}>C_6H_3:O$$

Eurhodol.

Amido-phenazines: a. *Monamido-phenazines*, the eurhodines, are produced (1) analogously to the parent substances, from amidated o-diamines and quinones:

$$\underset{\text{Triamido-benzene}}{NH_2.C_6H_3<{NH_2 \atop NH_2}} + \underset{\beta\text{-Naphthoquinone}}{\begin{matrix} OC-CH=CH \\ | \qquad\qquad | \\ OC-\!\!-\!\!-\!\!-C_6H_4 \end{matrix}} \longrightarrow \underset{\text{Amidophenonaphthazine.}}{NH_2C_6H_3<\begin{matrix} N-C-CH=CH \\ | \quad \| \qquad\quad | \\ N-C-\!\!-\!\!-\!\!-C_6H_4 \end{matrix}}$$

(2) By the action of aromatic monamines upon o-amidoazo-bodies:

$$C_7H_6<{N:NC_7H_7 \atop NH_2} + C_{10}H_7NH_2 \longrightarrow C_7H_6<{N \atop N}>C_{10}H_5NH_2(+C_7H_7NH_2+H_2).$$

(3) By the condensation of quinone dichlorimides or p-nitroso-dimethyl aniline with monamines, in which the p-position is occupied (if this be free, indamines result, p. 174):

$$\underset{\text{Nitrosodimethylaniline}}{(CH_3)_2N.C_6H_3<{NO \atop H}} + \underset{\beta\text{-Naphthylamine}}{{H \atop NH_2}>C_{10}H_6} \longrightarrow \underset{\text{Dimethylamidophenonaphthazine.}}{(CH_3)_2NC_6H_3<{N \atop N}>C_{10}H_6}$$

The eurhodines are feeble bases. Their salts are scarlet red in color. They dissolve in concentrated sulphuric acid with a carmine-red color, which, upon the addition of water, passes successively into black, green, and finally red, which is due to the gradual dissociation of polybasic salts, only stable in the presence of concentrated acids. The ethereal solutions have a yellow-green fluorescence. If they be heated with acids, they become oxyphenazines. They are not applicable technically.

Amidophenazine, $C_6H_4(N_2)C_6H_3NH_2$, has been prepared from o-diamidophenazine upon heating it with zinc-dust. It results in the oxidation of the diamidodipenylamines, $NH_2[2]C_6H_4NHC_6H_4[3]NH_2$, or $(NH_2)_2[2,4]C_6H_3NHC_6H_5$ (B. **29**, 1874). It consists of red bronze needles that melt at 265°.

b. Unsym. *diamidophenazines* are formed in the oxidation of o-diamines (p. 95):

$$C_6H_4<{NH_2 \atop NH_2} + C_6H_4<{NH_2 \atop NH_2} \xrightarrow{O} \underset{\text{Unsym. Diamidophenazine.}}{C_6H_4<{N \atop N}>C_6H_2<{NH_2 \atop NH_2}}$$

c. Sym. *diamidophenazines, Toluylene-red Group:* Symmetrical diamidophenazines are produced when amidated indamines are oxidized (p. 174):

$$NH:C_6H_3<{NH_2 \atop N}>C_6H_4NH_2 \xrightarrow{O} \underset{\text{Sym. o-Amidophenazine.}}{NH_2C_6H_3<{N \atop N}>C_6H_3NH_2}$$

Instead of using the prepared indamine, a mixture of a p-diamine with a m-diamine may be oxidized, or quinone chlorimides may be allowed to act upon a m-diamine. Thus, **tolulyene-red, dimethyldiamidotoluphenazine**, $NH_2C_7H_5N_2C_6H_3N(CH_3)_2$, is produced by oxidizing dimethylparaphenylenediamine with m-toluylenediamine (p. 95). Toluylene-blue appears as an intermediate product (p. 174).

It crystallizes in orange-red needles. It is applied in dyeing under the name *Neutral Red*. Its monacid salts are rose-red in color; the diacid, blue; and the triacid, green; the last two are stable only in the presence of strong acids. It colors silk and cotton, mordanted with tannin, a scarlet-red. It yields *dimethylmonamidotoluphenazine* by deamidation.

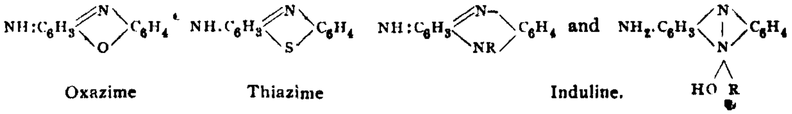
Oxyphenazines, *eurhodols*, are formed (1) when the amidophenazines are heated to 180° with concentrated hydrochloric acid; (2) synthetically, by condensing o-diamines with o-quinones containing hydroxyl. The eurhodols resemble the eurhodines in color and fluorescence.

α-**Oxynaphthophenazine**, $HOC_6H_8N_2C_6H_4$, from amidonaphthophenazine or produced by the condensation of oxy-*β*-naphthoquinone with o-phenylenediamine, yields two isomeric *methyl ethers*—an oxygen and a nitrogen ether—corresponding to the two formulas presented (p. 599) for eurhodol.

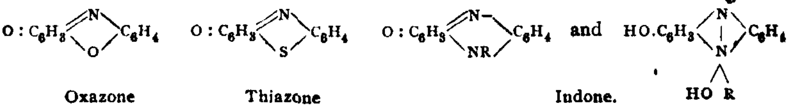
Dioxyphenazines are obtained similarly to the monoxy-bodies. The condensation of o-phenylenediamine with dioxydiketotetrahydronaphthalene (produced by the action of hypochlorous acid upon *β*-naphthoquinone) gives rise to **naphthophenazine oxide**, $C_6H_4N_2C_{10}H_6>O$. This is a body resembling ethylene oxide. Hydrochloric acid rearranges it into *β*-**oxynaphthophenazine**, $C_6H_4N_2C_{10}H_5OH$, melting at 198° (B. **26**, 617; A. **286**, 61).

Azonium Compounds: These are important because they are to be regarded as the parent substances of the dyestuffs of the induline, indone, and safranine series, from which they are produced by diazotizing in strongly acid solution, and to which they revert upon treatment with ammonia or alkalies. See p. 597 for their synthetic methods of formation. The phenylazonium salts have been chiefly isolated by means of their *ferric chloride double salts*. **Ethyl Phenazonium Iodide, Methyl Naphthophenazonium Iodide**, $C_6H_4(N_2.C_2H_5I)C_6H_4$ and $C_{10}H_6(N_2CH_3I)C_{10}H_6$, are produced by the union of the corresponding azines and alkyl iodides (B. **30**, 391). **Phenyl Phenazonium Chloride** results from the de-amidation of aposafranine chloride. The *ferric chloride double salt*, $C_6H_4(N_2C_6H_5.Cl)C_6H_4.FeCl_3$, melts at 186°. **Phenyl Naphthophenazonium Chloride**, $C_{10}H_6(N_2C_6H_5.Cl)C_6H_4$, is obtained from rosinduline and isorosinduline (p. 601). An isomeric **Isophenyl Naphthophenazonium Chloride** has been prepared from *ψ*-rosinduline (p. 601) and also by condensation of *β*-naphthoquinone with phenyl-*o*-phenylenediamine (B. **29**, 2316, 2967).

Indulines, Indones, and Safranines.—These dyestuffs sustain the same relation to the phenazines as the oxazines and oxazones (p. 580) to phenoxazine, and the thiazines and thiazones to thiodiphenylamine (p. 583). They are quinone-anils, indamines, and indophenols (p. 173), in which the two aromatic nuclei are further linked to each other by the group NR; hence, they are to be considered as meso-alkyl- or alphyl-derivatives of the paraquinoïd forms of the eurhodines and eurhodols (p. 599). However, the induline salts can be converted, by means of their diazo-bodies, through de-amidation, into *azonium salts* (p. 598), and would therefore have to be viewed as amidated azonium salts; but the corresponding azonium hydrates appear, however, to part readily with water and then pass into the paraquinoïd forms (B. **29**, 2316, 2752, 2771):



Oxazime Thiazime Induline.



Oxazone Thiazone Indone.

To save space, the paraquinoïd formulas for the bases are mostly employed; they will be readily understood from what has been expressed above. The radical (R) may be an alkyl- or an alphyl-group. The

phenylated derivatives primarily are important technically (A. **286**, 187; B. **28**, 1579).

The *indulines* are prepared universally (1) by heating p-amidazo-bodies with monamines in the presence of some mineral acid:

$$NH_2[4]C_6H_4N:NC_6H_5 + C_6H_5NH_2 \longrightarrow NH:C_6H_3\begin{matrix}\diagup N \text{———} \diagdown \\ \diagdown N(C_6H_5) \diagup\end{matrix}C_6H_4.$$

The intermediate and by-products in this reaction are p quinone di imide derivatives—*e. g.*, quinone dianil, anilidoquinone dianil, dianilidoquinone dianil, or azophenine (p. 173), etc. They are to be considered as the real generators of the indulines (B. **25**, 2731). Thus, quinone dichlordiimide and phenyl-β-naphthylamine form isorosinduline (B. **29**, 2753):

$$ClN:C_6H_4\begin{matrix}\diagup NCl \\ \; \end{matrix} + \begin{matrix} \; \\ HN(C_6H_5)\diagup \end{matrix}C_{10}H_7 \longrightarrow NH:C_6H_3\begin{matrix}\diagup N \text{———} \diagdown \\ \diagdown N(C_6H_5) \diagup\end{matrix}C_{10}H_6.$$

(2) Indulines and indones result from the condensation of oxyquinones and amidoquinones with phenylated o-diamines (B. **28**, 1714; A. **290**, 262):

$$\begin{matrix}O\diagdown \\ HO\diagup\end{matrix}C_6H_2\begin{matrix}\diagup OH \\ \diagdown O\end{matrix} + \begin{matrix}(C_6H_5)NH\diagdown \\ H_2N\diagup\end{matrix}C_6H_4 \longrightarrow \begin{matrix}O\diagdown \\ HO\diagup\end{matrix}C_6H_2\begin{matrix}\diagup N(C_6H_5)\diagdown \\ \diagdown N \text{———} \diagup\end{matrix}C_6H_4;$$

$$AcNHC_{10}H_5\begin{matrix}\diagup O \\ \diagdown O\end{matrix} + \begin{matrix}C_6H_5NH\diagdown \\ H_2N\diagup\end{matrix}C_6H_4 \longrightarrow AcN:C_{10}H_5\begin{matrix}\diagup N(C_6H_5)\diagdown \\ \diagdown N \text{———} \diagup\end{matrix}C_6H_4.$$

Indones are formed when the indulines are heated with concentrated mineral acids.

The indulines are among the longest known aniline dyestuffs (Caro and Dale, 1865; Griess and Martius, 1866). Their constitution has been made more evident by a series of investigations prosecuted in recent years by Fischer and Heppe, Kehrmann, Nietzki, etc. (A. **272**, 306; **290**, 247; B. **29**, 1442, 2318, 2771).

The indulines are classified:

1. **Benzo-indulines**, . . $NH:C_6H_3(N_2C_6H_5)C_6H_4$, from phenazine.
2. a. **Isorosindulines**, . $NH:C_6H_3(N_2C_6H_5)C_{10}H_6$ } , from naphtho-phenazine.
   b. **Rosindulines**, . . $NH:C_{10}H_5(N_2C_6H_5)C_6H_4$ }
3. **Naphthindulines**, . $NH:C_{10}H_5(N_2C_6H_5)C_{10}H_6$, from naphthazine.

The ms-*alkyl* derivatives, corresponding to these ms-phenyl-compounds, have also been prepared in various ways (see B. **30**, 394, etc.).

The benzo-indulines and iso-rosindulines, on the one side, being derivatives of benzoquinone, and the rosindulines and naphthindulines being derivatives of naphthoquinone, exhibit among themselves great similarity. The first two groups form violet to blue-colored, sparingly soluble salts. Their application in calico printing depends upon their solubility in *acetine* (I, 475) (*acetine print*). The ros- and naphth-indulines are strong bases. Their salts have an intense red color, and show red fluorescence. When their strongly acid solutions are diluted a change in color similar to that observed with the safranines occurs. The indulines, like the quinones, readily yield anilido-compounds upon digestion with anilines. Similarly, the indones, when heated with alkalies, become oxy-indones. See the safranines for the action of ammonia upon the indulines.

Benzene Induline, Aposafranine, $C_{18}H_{12}N_3$, results by de-amidation of phenosafranine. Further de-amidation yields the phenylphenazonium salt, which regenerates aposafranine by treatment with ammonia. Aposafranine, digested with aniline, forms **anilido-aposafranine** (B. **28**, 1709; **29**, 2967). Benzene induline is also obtained from p-amidoazobenzene and aniline. **Amidophenyl benzene induline,** $NH_2C_6H_4.N:C_6H_3(N_2C_6H_5)C_6H_4$, melting at 150°, is a side-product. By de-amidation it yields *phenylbenzene induline*. If p-amidoazobenzene be heated with p-phenylene-

diamine, a mixture of various amidoindulines is produced, and these form *paraphenylene blue*, a prized cotton dyestuff (A. **286**, 195).

Isorosinduline, $C_{10}H_6(N_2C_6H_5)C_6H_3 : NH$, from quinone dichlorimide and phenyl-β-naphthylamine, becomes phenylnaphthophenazonium (B. **29**, 2753) by de-amidation. Its *dimethyl* derivative is obtained from p-nitrosodimethyl aniline with aniline and α-naphthylamine. *Basler Blue* (A. **272**, 311) is an anilido derivative of this compound.

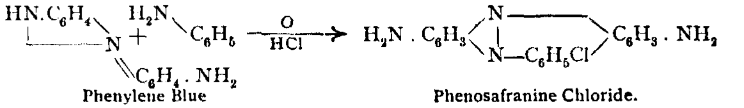
Rosinduline, $NH : C_{10}H_5(N_2C_6H_5)C_6H_4$, melting at 199°, is formed from benzene-azo-α-naphthylamine and aniline, from o-oxy-α-naphthoquinone-imide and o-amido-diphenylamine, as well as from 4-acetamido-o-naphthoquinone and phenyl-o-phenylene-diamine. **ψ-Rosinduline,** an isomeride, is also produced by the last method. It differs from rosinduline in the position of the $N . C_6H_5$-group with reference to the naphthalene nucleus (B. **24**, 2167; A. **290**, 262).

Rosinduline and isorosinduline by de-amidation are converted into phenylnaphthophenazonium salts, which regenerate rosinduline with ammonia. **Phenyl Rosinduline** melts at 235°. *Azocarmine* is its disulphonic acid (D. R. P., 45,370).

Naphthinduline, $NH : C_{10}H_5(N_2C_6H_5)C_{10}H_6$, melts at 250°. It is obtained from benzene-azo-α-naphthylamine with naphthylamine and aniline (A. **262**, 262; **272**, 311). *Naphthyl violet* is its anilido-derivative. *Naphthyl Blue* is the anilido-derivative of phenyl naphthinduline; it is produced by the inner condensation of benzene-azo-α-naphthylphenylamine.

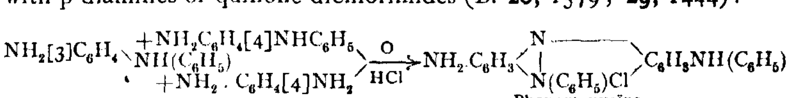
Rosindone, $O : C_{10}H_5(N_2C_6H_5)C_6H_4$, of the *indones* (see A. **286**, 242), occurs in the form of its sulphonic acid as a ponceau-red dyestuff having technical application. **Isorosindone,** $C_{10}H_6(N_2C_6H_5)C_6H_3 : O$, melting at 224°, is also obtained from nitrosophenol and phenyl-β-naphthylamine (B. **29**, 2755).

Safranines: Safranine salts should be regarded as *symmetrical di-amido-derivatives of the azonium salts,* as the unsymmetrical structure formerly proposed for these compounds has been abandoned by all investigators who have been active in this domain of research (B. **29**, 1442). They are produced (1) upon oxidizing a mixture of an indoamine and a monamine:



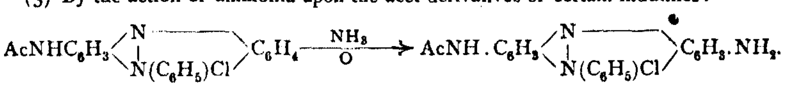
Phenylene Blue — Phenosafranine Chloride.

(2) By oxidizing a mixture of m-amido-derivatives of diphenylamine with p-diamines or quinone dichlorimides (B. **28**, 1579; **29**, 1444):



Phenomauveïne.

(3) By the action of ammonia upon the acet-derivatives of certain indulines:



The safranines usually form monacid, red-colored salts. The solutions in concentrated sulphuric or hydrochloric acids are green in color. Upon dilution they become blue, then red (dissociation of unstable polyatomic salts; compare the eurhodines, p. 599). The reverse in color-change occurs upon adding acid to the dilute salt solutions. The sparing solubility of their nitrates is noteworthy. The alcoholic solutions usually

exhibit a strong yellowish-red fluorescence. Views in regard to the structure of the free bases have been proposed. Reducing agents convert safranines into leuco-compounds, which in the presence of alkalies are rapidly reoxidized by the air to safranines.

The lowest member of the safranines is—

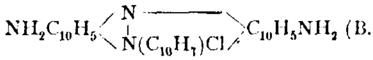
Phenosafranine, $C_{18}H_{15}N_4Cl$. It consists of leaflets, green in color, or of steel-blue needles. Baryta separates *safranol.*

When its monodiazo-compound is boiled with alcohol, aposafranine chloride is produced; the acetyl derivative of the latter, upon treatment with ammonia, again yields an acetyl phenosafranine (B. 30, 1565). Unsym. **dimethyl-** and **diethylphenosafranines** (B. 28, 1356) are obtained from dimethyl- and diethyl-p-phenylenediamine with two molecules of aniline. Dimethylphenosafranine is the basis of the dyestuff *fuchsia. Giroflé* of commerce is an homologue. n-**Tetraethylphenosafranine** is the violet dyestuff *amethyst.*

Tolu-safranine, $C_{18}H_{13}(CH_3)_2N_4Cl$, from toluylenediamine, o-toluidine (1 molecule) and aniline (1 molecule), is the chief constituent of common *safranine*, occurring in commerce as a brown paste or yellow-red powder, employed in cotton and silk dyeing as a substitute for safflor. The necessary base-mixture for its production is obtained from the "aniline oil for safranine." This is partially diazotized and the product broken up into paratoluylenediamine and orthotoluidine by reduction.

Naphthophenosafranine Chloride, $NH_2C_{10}H_6(N_2C_6H_5.Cl)C_6H_3NH_2$. Its acetyl derivative is produced from acetyl rosinduline and ammonia (B. 30, 1566).

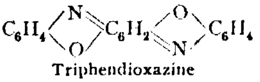
The dyestuff **indazine,** $C_6H_5NHC_6H_3(N_2Cl C_6H_5)C_6H_3N(CH_3)_2$, is closely allied to the safranines in its method of formation. It melts at 218°, and is obtained from diphenyl-n-phenylenediamine and nitrosodimethyl aniline. The analogous non-methylated body, from nitroso-aniline and diphenyl-m-phenylenediamine, or from m- and p-amidodiphenylmine, is identical with **Phenomauveïne,** which is closely related to **mauveïne,** the first aniline dye to prove valuable technically (Perkin, 1856). Mauveïne is produced by oxidizing aniline containing toluidine with potassium bichromate or lead peroxide. **Magdala Red** belongs to the safranines (Hofmann, B. 2, 412). It results from amidoazonaphthalene and α-naphthylamine hydrochloride. It probably has the following constitution:

 (B. 26, 2235; 30, 1567).

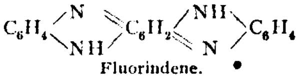
Safraninones and **Safranols** are to be viewed as sym. amido- and oxyderivatives of the indones. Like the safranines, they are prepared from m-oxydiphenylamines with nitrosodimethyl aniline or nitrosophenol (B. 28, 270, 503, 1354, 1578).

Safraninone, $C_{18}H_{13}N_3O$, and **Safranol,** $C_{18}H_{12}N_2O_2$, are made by boiling phenosafranine with baryta-water or caustic potash (B. 30, 399).

Fluorindenes: Fluorindene is the simplest representative of this class of dyestuffs. It corresponds to triphendioxazine (p. 580):

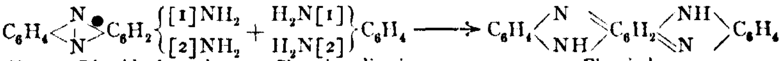


Triphendioxazine



Fluorindene.

The fluorindenes result by oxidizing or heating the salts of o-diamines; unsym. diamidophenazines appear as intermediate products (p. 600):



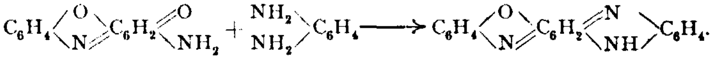
Unsym. Diamidophenazine o-Phenylenediamine Fluorindene.

The fluorindenes usually form green-colored crystals, which sublime without decomposition, and are sparingly soluble. Their solutions show a beautiful brick-red fluorescence.

Methyl Fluorindene, $C_6H_4 = (N_2H) \equiv C_6H_2 \equiv (N_2CH_3) = C_6H_4$, is obtained from the hydrochloride of diamidophenazine and methyl-o-phenylenediamine (B. 28, 395).

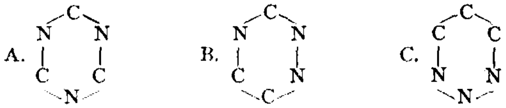
Phenyl Fluorindene, $C_6H_4N_2HC_6H_2N_2(C_6H_5)C_6H_4$, results from the condensation of aposafranine chloride (p. 601) with o-phenylenediamine (B. **29**, 367). **Diphenyl Fluorindene**, $C_6H_4 = (N_2C_6H_5) : C_6H_2 = (N_2C_6H_5) = C_6H_4$, is produced in the oxidation of azophenine, and also from phenylinduline by sublimation (B. **28**, 293).

Triphenazine Oxazine is a mixed oxazine-phenazine. It is formed from unsym-dioxyphenazine with o-amidophenol, or from amidophenoxazone with o-phenylenediamine (B. **28**, 299):



4. TRIAZINES.

Derivatives of the three possible metameric triazines are known:

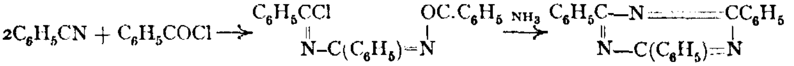


Sym. Triazine, Cyanidine   Unsym. (α)-Triazine   v-(β)-Triazine.

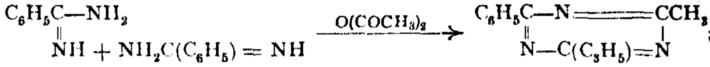
A. **Sym. Triazines, Cyanidines**: The formula of symmetrical triazine corresponds to the hypothetical *Trihydrocyanic Acid*, to which the metallo-hydrocyanic acids (1, 231) have been referred. Furthermore, a series of polymeric cyanogen compounds—*e. g.*, cyanuric acid, sulphocyanuric acid, cyanuric chloride, melamine, isomelamine, etc.—are derivatives of this triazine. They have already been discussed.

Alkyl- and *phenyl-derivatives* of sym. triazine or cyanidine are obtained:

1. By the action of aluminium chloride upon a mixture of benzonitrile and benzoyl chloride or acid chlorides. When benzoyl chloride is used, the reaction (best with the addition of ammonium chloride) proceeds as follows (B. **25**, 2263):



2. By the action of anhydrides of the fatty acids upon aromatic carbon-amidines (B. **25**, 1624):



carbonyl chloride acts the same as the anhydride of the fatty acid, with the production of oxycyanidines (B. **25**, 1424).

The cyanidines are weak, monacid bases. They are more or less readily decomposed into ammonia and carbonic acids.

Diphenyl Methyl Cyanidine, $C_3(C_6H_5)_2(CH_3)N_3$, melting at 110°, is made from benzamidine and acetic anhydride. It is oxidized to *diphenylcyanidine carboxylic acid*, which loses water readily and becomes **diphenyl cyanidine**, $C_3(C_6H_5)_2HN_3$, melting at 75° (B. 23, 2382).

Triphenyl Cyanidine, Cyanphenine, $C_3(C_6H_5)_3N_3$, was first obtained from benzoyl chloride and potassium cyanate (Cloëz, 1859), then by the polymerization of benzonitrile with concentrated sulphuric acid; from benzonitrile, benzoyl chloride, and Al_2Cl_6 (see above), as well as by the action of sodium upon a mixture of cyanuric chloride and brombenzene (proof of constitution). Compare B. **29**, R. **1124**, for the action of sodium upon benzonitrile. Nascent hydrogen decomposes it into ammonia and lophine; compare the similar conversion of **Cyanur-triethyl**, *triethyl cyanidine*, into triethyl glyoxaline (B. **28**, R. 66). **Perchlortrimethyl Cyanidine**, $C_3(CCl_3)_3N_3$, melting at 96°, results from the polymerization of trichloracetonitrile.

Diphenyl Oxycyanidine, $C_3(C_6H_5)_2(OH)N_3$, melting at 289°, from benzenylamidine and $COCl_2$ (B. **23**, 163), forms a well crystallizing sodium salt. PCl_5 converts it into *diphenylchlorcyanidine*, melting at 139°, which behaves like an acid chloride. Thus, ammonia readily changes it into *diphenylamidocyanidine*, melting at 172°.

Methyl Dioxycyanidine,
$$\begin{array}{l} CH_3C - N = C(OH) \\ \quad \| \qquad\qquad\quad | \\ \; N - C(OH) - N \end{array}$$
, is obtained from acetyl urethane and urea (A. **288**, 318).

Diamido-cyanidines are also found in the guanamines, which are produced on heating guanidine fatty-acid salts or biguanide with fatty acids:

$$\begin{array}{l} NH_2C-NH_2 \\ \quad \| \\ N-C(NH_2)=NH \end{array} + HCOOH \longrightarrow \begin{array}{l} NH_2C-N=CH \\ \quad \| \qquad\quad | \\ N-C(NH_2)=N \end{array}$$

Biguanide — Diamidocyanidine, Formoguanine.

Piperyl Amido-cyanidine, $C_3(NC_5H_{10})(NH_2)HN_3$, melting at 194°, is similarly obtained by heating piperyl guanide with formic acid, or by treating it with chloroform and caustic potash, even at 0° (B. **25**, 525).

Normal cyanuric acid (1, 419) is a **trioxycyanidine**, cyanuric chloride is a **trichlorcyanidine**, melamine is **triamidocyanidine**, and ammelide and ammeline (1, 427) are **oxydiamido-** and **dioxyamidocyanidines**. Isocyanuric acid and its derivatives are to be regarded as derivatives of a triketohexahydrocyanidine.

B. Unsym. (α-)-**Triazines**.—But few derivatives of the simple ring are known: **1,2-Diphenyl-3-oxy-α-triazine**, $C_3(C_6H_5)_2(OH)N_3$, melting at 218°, is produced in the condensation of benzil with semicarbazide (B. **28**, R. 110):

$$\begin{array}{l} C_6H_5.CO \\ \qquad | \\ C_6H_5.CO \end{array} + \begin{array}{l} H_2N-CO \\ \qquad\; | \\ H_2N-NH \end{array} \longrightarrow \begin{array}{l} C_6H_5C = N-C(OH) \\ \qquad | \qquad\qquad \| \\ C_6H_5C = N-N \end{array}$$

n-*Phenyl*- and n-*phenyl*-n-*alkyl ketotetrahydro-α-triazines* are made by heating the unsym. phenylhydrazido-acetic acid ester (p. 127) with formamide and substituted formamides (B. **28**, 1228):

$$\begin{array}{l} COOR + RHNCHO \\ | \\ CH_2-N(C_6H_5)-NH_2 \end{array} \longrightarrow \begin{array}{l} CO-NR-CH \\ | \qquad\qquad \| \\ CH_2-N(C_6H_5)-N \end{array}.$$

n-Diphenyl Ketotetrahydrotriazine, melting at 205°, is obtained from formanilide. An isomeric **n-diphenyl ketotetrahydrotriazine**,
$$\begin{array}{l} CH_2 - N(C_6H_5) - CH \\ | \qquad\qquad\qquad \| \\ CO - N(C_6H_5) - N \end{array}$$
, melting at 174°, has been prepared from anilido-acetic acid phenylhydrazide, $C_6H_5NHCH_2$-$CON(C_6H_5)NH_2$ (p. 127) with crystallized formic acid (B. **26**, 2616).

The derivatives of *benzo*- or *phen-α-triazine* are more numerous. They are produced (1) by the reduotion of sym. o-nitrophenylacidyl hydrazines:

$$C_6H_4\begin{array}{l}<NO_2 \quad COH \\ <NH-NH \end{array} \longrightarrow C_6H_4\begin{array}{l}<N = CH \\ <N = N \end{array}.$$

(2) By the condensation of formazyl compounds on boiling them with concentrated acids (B. **25**, 3206, 3540; **26**, 2788):

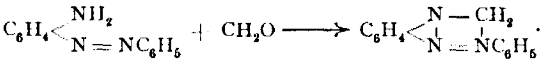
$$\begin{array}{l} C_6H_5N=N \\ C_6H_5NH-N \end{array}\!\!>CCOCH_3 \longrightarrow C_6H_4\begin{array}{l}/N=N \\ \backslash N=CCOCH_3 \end{array} (+ C_6H_5NH_2).$$

The phen-α-triazines are *yellow*-colored, crystalline compounds, having an alkaloid-like odor. They are very slightly basic.

Phentriazine, $C_6H_4(CN_3H)$, melting at 75° and boiling at 235–240°, results from the reduction of o-nitrophenylformylhydrazine, or by the exit of CO_2 and aniline from formazyl carboxylic ester. **Phenmethyl Triazine**, $C_6H_4[CN_3(CH_3)]$, melting at 89°

and boiling at 250–255°, is obtained from o-nitrophenylacetylhydrazine. **Phentriazyl Methyl Ketone,** $C_6H_4[CN_3(COCH_3)]$, melting at 114°, is derived from formazyl methyl ketone.

The *phendihydro-a-triazines* are related to the phen-*a*-triazines. They are obtained, instead of the expected alkylidene amido-derivatives (B. **24**, 1002, R. 948), from o-amido azo-compounds and aldehydes:



These compounds are *colorless*. They are feebly basic, stable bodies, which can be heated with hydrochloric acid to 150° without decomposition.

Tolu-n-tolyl-*a*-dihydrotriazine, $C_7H_6[CH_2N_3(C_7H_7)]$, melts at 178°. **Naphtho-*n*,*c*-diphenyl-*a*-dihydrotriazine,** $C_{10}H_6[CHN_3(C_6H_5)_2]$, *melting at 193°, is formed from* benzene-azo-*β*-naphthylamine and benzaldehyde.

C. *Phendihydro-β-triazines* are derived from adjacent *a*- or *β*-**Triazine.** They are ring homologues of the azimido benzenes, and are prepared from the o-amidobenzylamines and o-amidobenzamides with nitrous acid, just as the phendihydrometadiazines or dihydroquinazolines are obtained from the carboxylic acids (p. 590):

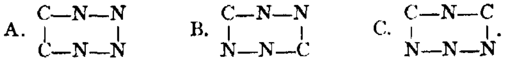
Phen-n-phenyl Dihydro-*β*-triazine, $C_6H_4[CH_2N_3(C_6H_5)]$, melts with decomposition at 128° (B. **25**, 445).

Phen-n-benzyl Dihydro-*β*-triazine, $C_6H_4[CH_2N_3(C_7H_7)]$, melts at 91° (B. **28**, R. 383).

Phenketodihydro-*β*-triazine, *Benzazimide*, $C_6H_4[CON_3H]$, melts with decomposition at 212°. It is formed when N_2O_3 acts upon o-amidobenzenylamidoxime (J. pr. Ch. [2], **37**, 432; **43**, 446; **48**, 92; B. **29**, 626; R. 785).

5. TETRAZINES.

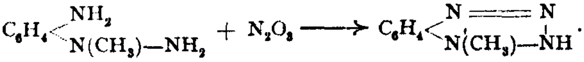
Only the first two of the three possible metameric tetrazine rings are known in certain derivatives:



A. The **osotetrazones** are derived from adjacent tetrazine. They result in the oxidation of the osazones, and are to be viewed as n-dialkyl- or dialphyl-dihydro-v-tetrazines:

They become triazoles if heated or if acted upon with hydrochloric acid and ferric chloride.

Phen-n-methyl Dihydrotetrazine, melting at 62°, is a *benzo-derivative* of v-tetrazine. It is formed when nitrous acid acts upon o-amidophenylmethylhydrazine, and corresponds to the phendihydro-*β*-triazines (J. pr. Ch. [2], **41**, 176):



The *isophendihydrotetrazines*, on the other hand, are constituted analogously to the

phendihydro-*a*-triazines. They result by the reduction of the diazo-salts of o-amido-azo-compounds (p. 115) (B. 19, 1457; 21, 543):

$$C_7H_6\begin{cases}N=NCl\\N=NC_7H_7\end{cases} \longrightarrow C_7H_6\begin{cases}N-NH\\|\quad\ \ |\\N-NC_7H_7\end{cases}$$

Azotoluene-o-diazochloride — Tolu-n-tolyldihydroisotetrazine, m. p. 168°.

B. Sym. **Tetrazine**, $\begin{array}{l}CH-N=N\\ \| \qquad\quad\ |\\ N-N=CH\end{array}$, yields several alphyl derivatives, which are characterized by their intense red color, and their stability toward acids, but which are decomposed by alkalies (B. 26, 2126; 27, 984, 3273):

Diphenyl Tetrazine, $C_2(C_6H_5)_2N_4$, forms bluish-red leaflets, melting at 192°. It is easily produced by oxidizing—

Dihydrodiphenyl Tetrazine, consisting of yellow needles. This is produced in the action of excessive hydrazine upon benzimido ether:

$$2\begin{array}{l}C_6H_5C=NH\\ \quad\ \ |\\ \quad\ OR\end{array} + 2NH_2NH_2 \longrightarrow \begin{array}{l}C_6H_5C=N-N=CC_6H_5\\ \qquad\ \ |\qquad\qquad\ |\\ \qquad NH\ —\ —\ NH\end{array}.$$

The dihydro-derivative is converted into tetrazine by heating, by moderated oxidants, and even by the oxygen of the air. It can be regained from the tetrazine by reducing the latter with zinc-dust and glacial acetic acid. If the body be boiled with these reagents, the reduction extends further: ammonia and *diphenyl triazole* (p. 512) are produced. When dihydrodiphenyl tetrazine is boiled with hydrochloric acid, it forms in part *diphenyloxybiazole* (p. 516) and in part it becomes the isomeric—

Isodihydrodiphenyl Tetrazine, $\begin{array}{l}C_6H_5C-NH-N=C.C_6H_5\\ \qquad\ \|\qquad\qquad\quad\ |\\ \qquad N\text{———————}NH\end{array}$, melting at 258°, which cannot be oxidized to a tetrazine. n-Derivatives of this body may be synthesized from aromatic hydrazines with chloroform and caustic potash:

$$\begin{array}{l}C_6H_5NH.NH_2\\ CHCl_3\end{array} + \begin{array}{l}CHCl_3\\ H_2N.NHC_6H_5\end{array} \longrightarrow \begin{array}{l}C_6H_5N\text{——}N=CH\\ \quad\ |\qquad\quad\ |\\ \quad CH=N-N.C_6H_5\end{array}.$$

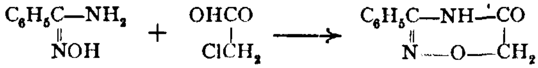
n-Diphenyl Isodihydrotetrazine, melting at 180°, is obtained by heating formyl phenylhydrazine (B. 30, 1263). **n-Ditolyl Isodihydrotetrazine** melts at 185° (B. 23, R. 250).

Urazine, *Bishydrazicarbonyl*, *Diurea*, $\begin{array}{l}HN\text{——}NH-CO\\ \ |\qquad\qquad\quad\ |\\ CO-NH-NH\end{array}$, melting at 270°, is a p-*diketohexahydrotetrazine*. It is produced when hydrazidicarboxylic ester or hydrazidicarbonamide, $NH_2.CO.NH.NH.CO.NH_2$, is heated with hydrazine. It is a strong, monacid base (J. pr. Ch. [2], 52, 482; C. 1897, II, 264. **Diphenyl Urazine**, $\begin{array}{l}C_6H_5N\text{——}NH-CO\\ \ \ |\qquad\qquad\quad\ |\\ CO-NH-N.C_6H_5\end{array}$, melting at 264°, is produced when phenylsemicarbazide, $C_6H_5NH.NH.CONH_2$, and phenylcarbazinic ester are heated, or when alkalies act upon diphenylcarbazidodicarboxylic ester (B. 21, 2329; A. 263, 282; B. 29, 829). An isomeric *diphenyl urazine* is formed when $COCl_2$ acts upon sodium phenylhydrazine (B. 26, R. 20).

6. ***Substances consisting of polyhetero-atomic six-membered rings, which contain O- and S-members, in addition to nitrogen, are not very numerous.*** Some are produced in reactions similar to those in which the corresponding five-membered rings are formed.

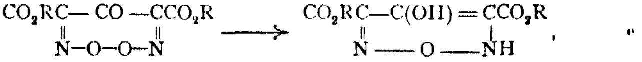
Just as the five-membered azoximes (p. 515) are prepared from the amidoximes and carboxylic acid chlorides, so their corresponding six-membered ring homologues are

prepared from amidoximes and α-chlor-fatty acids (B. **22**, 3161; **27**, 3353; **28**, 1374; **29**, 2656):



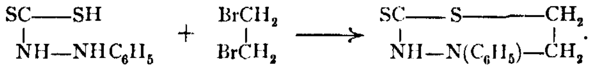
Benzenylamidoxime — Chloracetic Acid — Benzenylamidoxime-acetic Acid Isoanhydride, m.p. 148°.

The five-membered furazanes or azoxazoles (p. 514) have corresponding six-membered *azoxazine* derivatives. The reduction of diisonitrosoacetone dicarboxylic ester peroxide leads to **oxyazoxazine dicarboxylic ester**:

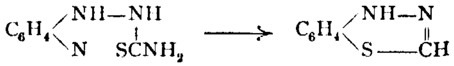


from which a series of additional azoxazine compounds has been prepared by rearrangement (B. **26**, 999).

The *thiodiazines* or *diazthines* are homologues of the thio-[b,b$_1$]-diazoles. An n-**phenylthiopentahydrodiazthine**, melting at 94°, is formed in the condensation of phenylsulpho-carbazinic acid with ethylene bromide (B. **27**, 2516):



Benzo-derivatives of the diazthines are produced when the phenylthiosemicarbazides are treated with hydrochloric acid (B. **27**, 861) (p. 128):



Phenylthiosemicarbazide — Benzodiazthine.

Benzodiazthine, *Phenylsulphocarbizine*, melting at 129°, is decomposed by fusion with caustic potash into o-amidothiophenol. **Benzo-n-methyldiazthine**, from unsymmetrical phenyl-methyl semicarbazide, and others behave similarly.

The **thialdines** (1, 203) contain a six-membered ring, with two S-members and one N-member. They are produced by the action of ammonia, etc., upon the trithioaldehydes.

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